

Assessment of the Detrex Source Control Remedy and DNAPL Migration Pathways to Fields Brook

Fields Brook Superfund Site Ashtabula, OH

Prepared for Fields Brook Action Group (FBAG)

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1 Introduction

The detection of DNAPL and associated contamination in Fields Brook over the last 5 years has led to a series of response/ remedial actions at the Fields Brook Superfund Site (Site). During this time period, two types of DNAPL have been found: a chlorinated VOC DNAPL attributable to Detrex and a PCB DNAPL attributable to Millennium Inorganics Corporation (MIC). DNAPL associated with the Detrex Facility has been found at multiple locations in Fields Brook and the DS Tributary, after soil and sediment remediation had been completed in the Sediment Operable Unit (SOU)/Floodplain Wetland Area (FWA) and source remedial measures required in the Source Control Operable Unit (SCOU) had been implemented. PCB DNAPL was encountered in the EU-8 portion of Fields Brook. Since 2005, the Fields Brook Action Group (FBAG) has undertaken a number of proactive measures to protect Fields Brook, ranging from sediment/soil removal to installation of DNAPL collection trenches. Finally, the FBAG recently relocated and reconstructed the EU-8 portion of the Brook in a manner that isolates Fields Brook and prevents recontamination from occurring. The reconstruction measures include subsurface DNAPL engineering controls to intercept any DNAPL that may otherwise reach the Brook. Furthermore, Detrex and MIC have installed interceptor trenches along portions of their properties abutting the EU8 to mitigate further DNAPL migration to this section of Field Brook.

The above-described actions being undertaken in EU-8 will provide long term protection to this section of Fields Brook. However, there are clear and compelling signs of continued Detrex DNAPL migration into EU6 and the DS Tributary: the presence of DNAPL in DS Tributary sediments (just west of State Road), DNAPL seepage at the North Sewer from 2005 onwards, and the findings of DNAPL in utilities in late 2008/ early 2009 (North Sewer, CEI conduit, a water line). These findings indicate that, conditions in originally "clean" sections of the DS Tributary and Fields Brook have considerably deteriorated since the initial remedial investigations and/or sediment/floodplain soil remedial actions were performed at the Site. If left unabated by Detrex, conditions at the Site will continue to deteriorate and DNAPL from the Detrex facility will continue to threaten EU-6 and downstream reaches of Fields Brook. Consequently, this report presents a discussion of the DNAPL migration mechanisms that are affecting EU6 and the DS Tributary, and an overview of the limitations of the Detrex source control remedial measures. Specifically, this report

- Presents a discussion of the Detrex SCOU ROD remedy, how the ROD's remedial
 objectives are not being met, and the reasons for the ineffectiveness of the Detrex
 remedy;
- Examines the chemical data and field observations associated with the DNAPL manifestations in the areas west and southwest of the Detrex facility (*i.e.*, DS Tributary, North Sewer, Other Utilities); and
- Analyzes the available data for the Detrex facility and presents an updated conceptual site
 model based on multiple lines of evidence for continued off-site migration of Detrex
 DNAPL.

FBAG strongly believes that Detrex needs to immediately implement supplemental source control measures and eliminate DNAPL migration pathways to Fields Brook.

2 Detrex Remedy – Elements and Causes of Ineffectiveness

Overall, the Detrex Source Control Remedy has been ineffective in reducing DNAPL volume at the source area (former lagoons) and in preventing DNAPL migration to Fields Brook. This chapter first presents an overview of the SCOU ROD requirements and then presents the reasons why the installed remedy has been ineffective.

2.1 Detrex SCOU ROD Requirements

The remedy implemented at the Detrex facility is significantly different from the SCOU ROD remedy and has failed to meet the ROD's remedial action objectives.

The SCOU ROD remedy for Detrex consisted of two central elements: 1) a source remediation component, intended to collect DNAPL and to remediate the source area; and 2) containment measures to prevent migration of DNAPL and contaminant migration into the DS Tributary and Fields Brook. Specifically, the SCOU ROD remedy required Detrex to install the following measures (also depicted in Figure 1).

Source Remediation System

Vacuum-enhanced extraction wells were envisioned "near the leading edge of the DNAPL plume near the slurry wall and within the plume to lower groundwater and collect DNAPL in source areas (US EPA, 1997, p. 62);"

Migration Control Measures

A slurry wall — Intended to be 1,500-feet long and to be installed "beyond the downgradient portion of the on-site and off-site DNAPL and dissolved COCs plume" (US EPA, 1997, p. 62). The ROD envisioned a slurry wall along the northern and western sections of the Detrex property, which were the "understood" groundwater flow and glacial till surface slope directions. In addition to the slurry wall serving as a physical barrier for DNAPL and contaminated groundwater migration, the ROD also envisioned using vacuum enhanced extraction wells to lower the groundwater table on the upgradient side of the slurry wall. Lowering the groundwater table was intended to maintain an inward hydraulic gradient and to further minimize contaminant migration — a standard and integral component of slurry-wall type containment systems (US EPA, 1997, p. 30):

- The...vacuum-enhanced extraction wells installed inside the slurry wall would lower the water table inside the slurry wall and reverse the flow of groundwater away from the slurry wall."
- ► "In addition, water level data would be collected to evaluate groundwater flows within the remedial response area."

The ROD also required compatibility tests between Detrex DNAPL and the slurry wall material to validate material compatibility.

DS Tributary Culvert – "In order to reduce the potential for subsurface water seepage to enter the DS Tributary in the northeast portion of the site, a 30-inch diameter culvert will be installed in the DS Tributary to contain surface water flow and keep groundwater from entering the stream flow. This culvert will connect to the existing culvert beneath State Road and will extend along the northern side of the railroad spur, approximately 600 feet upstream. This configuration will entirely contain the surface water in the DS Tributary north of the Detrex facility, seal off potential groundwater seepage and prevent soil erosion. All joints will be sealed to eliminate seepage. Sediment beneath the culvert will be excavated to a depth of approximately 2.0 feet (US EPA, 1997, p. 64)."

Collectively, these remedial measure were intended to put in place source control measures to prevent the continued migration of Detrex DNAPL into Fields Brook based on the original conceptual site model. However, a substantial amount of knowledge has been gained since that time, and two fundamental problems with the Detrex remedial measures are now apparent. First, the remedial measures required by the original ROD were not designed, installed and operated to meet critical performance needs; and second, the extent of the original SCOU remedial components do not address all DNAPL migration pathways identified in either the original or the updated conceptual site model.

Figure 2 depicts the as-built Detrex remedy, with passive groundwater interceptor trenches as the sole means of inducing an inward hydraulic gradient. Although the SCOU ROD remedy elements (*i.e.* source remediation, slurry wall, DS Tributary containment) were, to a limited extent, implemented, the Detrex remedy has failed to meet the ROD objectives. As described in greater detail below, the source remediation system has never been expanded beyond a small, poorly designed and poorly operated pilot-scale system, and the slurry wall is less than one third of the length specified in the ROD. Furthermore, we are unaware of any performance data collected to evaluate whether the groundwater interceptor trenches installed near the slurry wall and DS Tributary are effective in reversing the flow gradient over its limited length and preventing contaminants from entering the DS Tributary. To the contrary, observations of DNAPL in the DS Tributary point to a serious deficiency in the system.

2.2 Source Remediation Ineffectiveness

The Detrex source remedy has not been effective in recovering DNAPL due to ineffective system design and poor O&M practices.

The current Detrex Source Control system is under-sized, poorly designed, and does not utilize EPA-recommendations/Best Practices for Soil Vapor Extraction/Dual Phase Extraction (SVE/DPE) systems, as discussed in detail in our previous letter (included as Attachment 1). This system is still only at pilot scale and has never been properly evaluated or optimized.

- The system was improperly designed, inappropriate equipment was installed (e.g. small diameter wells, no air injection wells, the wrong vacuum blower) and there are too few wells to achieve adequate spatial coverage of the DNAPL plume.
- The system is operated on an intermittent basis and collects only liquids an inefficient approach for remediating a VOC-dominant DNAPL that is best remediated by vapor removal.
- DNAPL continues to flow into wells and accumulates to more than 10 feet thick in the Detrex source area. Greater than 15,000 gallons of DNAPL has been removed in

- approximately 6 years of operation with this limited and ineffective system, demonstrating the enormity of the DNAPL source area and that appreciable DNAPL recovery is possible.
- Detrex has proposed some modifications (enhancements) to the source remediation system. However, the proposed system modifications are inadequate and rely on a passive approach to DNAPL collection, which is not expected to be effective (see Attachment 1 for additional details).

It is widely acknowledged that source removal and remediation is a critical component of DNAPL remediation. This is especially relevant to the Detrex facility where a significant volume of DNAPL is still present. Despite this, the source control measures at the Detrex facility have been limited in scope and poorly implemented. Thus, it is clear that Detrex needs to avail of more effective technologies and operational experience to address DNAPL source removal at the facility.

2.3 Migration Control Ineffectiveness

Migration control elements of the Detrex Remedy do not satisfy the SCOU ROD requirements and have not been effective in preventing DNAPL migration.

As previously discussed, the Detrex SCOU ROD consisted of two containment measures: 1) the slurry wall and associated groundwater collection system; and 2) the DS Tributary containment *via* a DS Tributary Culvert. The slurry wall was intended to serve as a physical barrier for DNAPL and contaminated groundwater migration. The ROD also envisioned using vacuum enhanced extraction wells to lower the groundwater table on the upgradient side of the slurry wall to lower the groundwater table, and to maintain an inward hydraulic gradient to further minimize contaminant migration. Additionally, the ROD specified configuration of the DS Tributary Culvert was intended to entirely contain the surface water in the DS Tributary north of the Detrex facility, seal off potential groundwater seepage, and prevent soil erosion.

Slurry Wall

There are several major problems with the slurry wall placement and design:

- 1. The SCOU ROD correctly required that the wall be installed "beyond the downgradient portion of the on-site and off-site DNAPL and dissolved-phase COCs plume." These design criteria were specified to ensure that contaminated groundwater and DNAPL could be contained and captured to prevent contaminants from entering the DS Tributary and Brook. The slurry wall does not meet these design criteria because DNAPL was encountered within the slurry wall excavation during its installation. That is, the wall is not "located outside of DNAPL" as required by the ROD.
 - Compatibility tests between the Detrex DNAPL and the slurry wall material were also never conducted and the integrity of the wall has never been evaluated. Since the wall is within the DNAPL plume, material compatibility is a major concern.
- 2. The slurry wall envisioned by the SCOU ROD was large enough to contain groundwater and DNAPL migration northwest, west, and southwest of the Detrex plume (Figure 1). Detrex installed a slurry wall less than one third the length anticipated by the ROD and oriented the slurry wall to prevent only westward migration of DNAPL and contaminated

- groundwater (Figure 2). Therefore, there are significant gaps in the Detrex migration controls northwest and southwest of the DNAPL plume defined in the 1997 ROD.
- 3. For the slurry wall to serve as an effective barrier for DNAPL and groundwater migration, it is critical that an inward groundwater flow gradient be maintained - a fact acknowledged and required by the SCOU ROD. However, the system O&M reports do not present groundwater extraction flow rates or groundwater elevation data near the slurry wall to evaluate the trench's effectiveness, even though these measurements were required by the ROD. Consequently, there is no way of knowing whether groundwater elevations are being lowered adequately near the slurry wall to generate an inward flow gradient and prevent DNAPL and groundwater migration. The current groundwater interceptor trench functions as a passive (or gravity) drain, an approach that is much less effective at inducing an inward flow gradient than an active system, such as the vacuumenhanced extraction wells envisioned in the ROD. Passive drainage is slow, especially through the low permeability soils present at the site, resulting in a much smaller zone of influence localized around the trench than would be expected for an active extractionwell system. Moreover, any mobile DNAPL deeper than the bottom of the interceptor trench is not being captured by the current system.

DS Tributary

In order to prevent contaminants from entering the DS Tributary, the ROD required that the stream in the north-western portion of the Detrex facility be entirely contained in a 30-inch diameter culvert. Sediments were to be excavated to a depth of 2 feet and the seams in the culvert were to be sealed in order to prevent DNAPL, contaminated groundwater, and eroded soil/sediment from entering the stream.

To the best of our knowledge, no data have been collected to evaluate whether the installation of the culvert and a groundwater collection trench underneath the DS Tributary were effective in preventing seepage of DNAPL and/or contaminated groundwater into the DS tributary. The collection trench/culvert system does not appear to extend 600 feet upstream of State Road, as required by the ROD, and thus, does not likely contain the upstream portions of the DS Tributary adjacent to the leading edge of the Detrex plume (indicated in blue color on Figure 2). As described in the next chapter, the measured soil concentrations in soils on both sides of the DS Tributary in this area (on the RMI property) indicate that DNAPL is present in this area, and with no containment measures in place, DNAPL could be entering the DS Tributary in this area. Once DNAPL enters the stream, it could travel through the DS Tributary culvert and accumulate west of State Road. The presence of "new" DNAPL west of State Road in DS tributary sediments (i.e., post-remediation) could be attributable to this DNAPL migration pathway or due to leaks in the culvert.

3 Detrex DNAPL Manifestations – Western Area

The clearest indications of source control failure at the Detrex property are visual observations of DNAPL seeps. Detrex DNAPL seeps have been found in soils and sediments near numerous preferential migration pathways since 2005 (*i.e.* after the initial remediation was complete).

3.1 DS Tributary

The DS Tributary originates northeast of the Detrex property, then meanders southward where it crosses onto the Detrex property, and proceeds west, through the slurry wall and under State Road (Figure 2). As discussed above and indicated on Figure 2, the DS Tributary appears to be uncontained upstream of the groundwater interceptor trench.

Pooled DNAPL was first found in the sediments of the DS Tributary (EU5) in 2005, just west of State Road (de maximis, 2005), and has since been repeatedly observed in surficial sediments in this area. The visual presence of DNAPL was not identified in this area during the initial remediation in 2001 or in prior years, thus indicating that the absence of effective source control at the Detrex facility has resulted in DNAPL contamination of sediments and surface water in the DS Tributary. This is further corroborated by results of sediment sampling in 2008, which indicated that the highest COC concentrations in brook sediments, some exceeding remedial action levels (RAL), were present in this section of the DS Tributary (Table 1). During the initial remediation in 2001, contaminant concentrations did not exceed RALs. The recent observations of DNAPL pooling in the streambed and recent RAL exceedances clearly indicate that DNAPL has migrated into this area – a location where it previously was absent (US EPA, 2009, pg. 19).

3.2 North Sewer

The North Sewer runs parallel to and just west of State Road. The pipe underlies the DS Tributary, is submerged below the water table, and slopes southward to Fields Brook (Figures 2 and 3). The North Sewer discharges to Fields Brook at the edge of the Detrex SCOU, well above the brook water level (Figure 5a). Repeated DNAPL observations at the North Sewer have occurred since their initial discovery in 2005. These repeated observations over such an extended period of time strongly indicates the presence of pooled DNAPL in the Detrex source area, since "pooled DNAPL is susceptible to mobilization" whereas "disconnected blobs and ganglia" of DNAPL, referred to as residual DNAPL, are "trapped by capillary forces" and do not flow and persist in this manner (Kueper and Davies, 2009).

DNAPL seeps were initially observed at the North Sewer outfall during a site reconnaissance in 2005 (de maximis, 2005) and continued until 2007 when FBAG installed a DNAPL collection trench at the end of the North Sewer to prevent DNAPL from entering Fields Brook. Although it not known when DNAPL surface manifestations at the North Sewer began, DNAPL seeped from the North Sewer into the brook for at least the two years. Similar to the DS tributary, conditions at the North Sewer outfall at Fields Brook appear to have deteriorated, rather than improved, since source control remedial efforts were undertaken at the Detrex facility.

After the collection trench was installed at the North Sewer in 2007, groundwater samples were collected from the trench and analyzed for DNAPL components. According to US EPA (USEPA, 1992), the presence of a component of a DNAPL mixture in groundwater at a concentration greater than 1% of its

effective aqueous solubility typically indicates the presence of DNAPL. Detrex DNAPL marker compounds were found in excess of this limit during two different sampling events, indicating that DNAPL was accumulating in the sump (see Attachment 4 for details).

DNAPL was also observed at the North Sewer during the 2009 State Road Bridge replacement work. During the removal of soils from the west side of State Road, black-colored DNAPL was observed to be flowing from under the North Sewer pipe into the excavation (Attachment 2). At this time, the North Sewer was found to be full of water and leaking (see Figure 6). In addition to these field observations, water and soil concentration data further indicate the presence of a significant volume of DNAPL in and around the North Sewer:

- The mixture of water and DNAPL (18,000 gallons) that accumulated in the excavation at the North Sewer was pumped into a frac tank and sampled. These water samples were super-saturated (>100% of their effective solubility) with several Detrex DNAPL marker compounds, meaning globules of DNAPL were present in the frac tank (Table 2). The detection of elevated concentrations of Detrex marker compounds in the water samples is particularly significant, given the high degree of contaminant dilution expected in the large frac tanks (i.e. 18,000 gallons of water).
- Soils excavated at the North Sewer and north footer of the bridge were combined into a pile and sampled (Pile A, Table 3). Soil concentrations of several Detrex marker compounds indicated the presence of DNAPL in the pile (*i.e.* exceeded the C_{sat} threshold described in Chapter 4). These high concentrations of Detrex marker compounds were found despite the mixing of clean and contaminated soils (*i.e.* dilution was significant).

Overall, DNAPL seepage at the North Sewer for a prolonged time period, after Detrex source control measures had been implemented, is a clear indication of ongoing DNAPL migration and that conditions are continuing to deteriorate.

3.3 CEI Conduit

The CEI Conduit is located east of State Road, parallel to the North Sewer, and is also submerged beneath the water table (Figures 2 and 3). Similar to the North Sewer observations, DNAPL has been observed along the CEI conduit repeatedly over a long period of time, further corroborating ongoing DNAPL migration from the Detrex source area.

Initial DNAPL observations in the CEI conduit were reported in 1996 by a Centerior Energy employee who was overcome by VOC vapors while performing maintenance in a CEI conduit vault. Subsequently, an incident report was filed, which described chlorinated VOC vapors and contaminated groundwater in the vault. The workers attempted to pump out the liquid, "but ceased pumping when [the] pollutant continued to enter [the] vault from [the] surrounding area (Attachment 3)." Thus, DNAPL and contaminated groundwater was not only pooling in the vault, but actively flowing into it.

DNAPL and contaminated groundwater and soil were encountered in and around the CEI conduit again during the 2009 State Road Bridge replacement work. When excavation work on the east side of State Road exposed the CEI conduit, a significant volume of water was released from the conduit into the excavation. Contaminant concentrations in the accumulated water and surrounding soils indicated the presence of DNAPL:

- Approximately 10,000 gallons of water, which accumulated in the excavation in this area, was pumped to a frac tank and sampled. This water exceeded the 1% effective aqueous solubility limit for several Detrex marker compounds, indicating the presence of DNAPL (Table 2).
- The soils excavated from the east side of State Road in the vicinity of an observed DNAPL seep were piled and sampled. Soil concentrations for several chlorinated VOCs in this pile exceeded soil saturation thresholds, indicating that DNAPL was present in the pile (Pile B, Table 3).

Similar to the North Sewer, presence of DNAPL within the CEI conduit is an indication of ongoing DNAPL migration from the Detrex source area.

3.4 Water Line

A water line parallels the CEI conduit, but is located at a slightly higher elevation (Figures 2 and 3). Detrex DNAPL was observed seeping out of the bedding and fill around the water line during the 2009 State Road Bridge replacement work. In general, Detrex DNAPL was ubiquitous throughout this bedding/fill (see Attachment 2 for details). A DNAPL-containing sand seem was also found at the same elevation as the water line, demonstrating that multiple preferential pathways work in concert to facilitate DNAPL migration towards the brook.

4 Data Analysis and Conceptual Site Model

4.1 Interpretation Framework

The data collected within the Detrex source area clearly indicates the widespread presence of DNAPL throughout the source area and even downgradient (west) of the slurry wall (Figure 4). Thus, a large volume of DNAPL remains in the source area and provides a large driving head for outward DNAPL migration. Ongoing site investigations have revealed that soils, sediments, and groundwater far from the source area are contaminated with Detrex DNAPL components. Instead of comparing the detected concentrations to widely accepted DNAPL identification benchmarks (discussed below), Detrex and URS continue to rely on liquid DNAPL observations as the only means of DNAPL presence – a very narrow perspective for examining the data. Furthermore, it is now recognized that the original assumption that DNAPL releases to Fields Brook occurred solely or predominantly *via* releases to the Detrex outfall was incorrect. Evidence and knowledge gained during field work and assessments performed over the past decade indicate that there are multiple pathways for DNAPL migration from the DNAPL source area on the Detrex property to Fields Brook.

To fully assess the data collected at Fields Brook Site, the information must be interpreted using an appropriate framework that relies on multiples lines of evidence (and not just liquid DNAPL presence) (Kueper and Davies, 2009). There are two widely accepted, EPA-approved concentration benchmarks that the FBAG and Gradient have utilized to-date to interpret soil and water concentration data (Kueper and Davies, 2009; Attachment 5):

- C_{sat} Soil Concentration Benchmark. C_{sat} is the concentration of individual VOCs in soil that indicates the presence of DNAPL.
- C_{sol} Effective Aqueous Solubility Limit. C_{sol} is the effective solubility limit for individual compounds in a DNAPL mixture. The effective solubility of an individual compound depends on the DNAPL's composition (more precisely, the mole fraction of each compound in the bulk DNAPL), commonly known as Raoult's law. According to US EPA (USEPA, 1992), the presence of a component of a DNAPL mixture in groundwater at a concentration greater than 1% of its effective aqueous solubility typically indicates the presence of DNAPL.

The FBAG and Gradient have used these benchmarks to clearly show that DNAPL is present throughout the western Detrex property (Attachment 4). The FBAG and Gradient have further refined this indicator approach and developed another soil concentration benchmark, C_{mobile} , which indicates the presence of mobile DNAPL (Wiedemeier *et al.*, 1999; Attachment 5). All of these benchmarks are technically valid and widely accepted by the scientific community, although C_{mobile} has several advantages over the other approaches for assessing data at the Fields Brook site.

- C_{mobile} indicates that DNAPL is <u>mobile</u> whereas C_{sat} and C_{sol} merely indicate that DNAPL is present. Many of the current issues at the Detrex property relate to concerns over DNAPL mobility since DNAPL is already known to be present at the Detrex facility.
- C_{mobile} applies to fractured clay as well as granular soils (*i.e.* gravel, sand, and silt), whereas C_{sat} is not appropriate for fractured clay. Since fractured clay is the dominant soil type at Fields Brook, C_{mobile} , is particularly relevant at the Site.

• C_{mobile} is a benchmark for total VOCs in soil and makes no assumptions about the DNAPL's chemical composition, whereas C_{sat} and C_{sol} are benchmarks for individual VOCs and are a function of the DNAPL's chemical composition.

The C_{mobile} benchmark for fractured clays at Fields Brook was calculated to be 13 mg/kg total VOCs (see Attachment 5 for details), meaning that any exceedance of this benchmark indicates potentially mobile DNAPL.

4.2 Conceptual Site Model

DNAPL continues to migrate from the former Detrex lagoon area *via* multiple preferential pathways and threaten the downstream (off-site) portion of the DS Tributary and EU6 of Fields Brook.

In order to effectively protect Fields Brook from recontamination with DNAPL, an understanding of DNAPL migration from source areas to the brook is critical. A thorough review of the available soil database indicates that there are C_{mobile} exceedances throughout the Detrex source area, beyond the slurry wall, and along several preferential migration pathways (Figures 3 through 5a/b). Additionally, C_{mobile} exceedances have occurred over a broad depth horizon, from the DS Tributary surface sediments (Figure 3) to a depth of more than 25 feet below ground surface in the Detrex lagoon area (Figure 4). The accumulated data collected in EUs 5, 6, and 8 conforms to a simple updated conceptual site model that is organized around three primary DNAPL migration pathways:

Pathway 1 – DS Tributary

The DS Tributary flows, largely uncontained, along the northern Detrex property boundary and through the slurry wall, thus providing a direct conduit for the pooled DNAPL on the Detrex facility to migrate beyond the source controls (slurry wall) and towards Fields Brook. The migration of DNAPL via this pathway is evident from the presence of pooled DNAPL found in the DS Tributary streambed west of State Road and detection of soil concentrations, indicative of mobile DNAPL, beneath the streambed and down to depths of the underground utilities (Figure 3). These underground utility pipes slope downward toward the brook, and thus, provide additional DNAPL migration conduits to the brook. The source of these DNAPL findings has recently been debated (i.e. historical versus recent migration), however, as described below, there is a clear mechanism that explains the DNAPL migration from the Detrex source area, through the DS Tributary culvert, to sediments west of State Road.

- The Detrex DNAPL plume, as defined in the 1997 ROD, extended onto the RMI property, not far from the DS Tributary. C_{mobile} exceedances (*i.e.* mobile DNAPL) have been found in soil borings on the RMI property on both sides of the DS Tributary (see DPT-7 and DETSB20 in Figure 5b). The recent finding of mobile DNAPL at DPT-7 suggests the possible expansion of the Detrex plume to the northwest and across the DS Tributary. This reach of the DS tributary appears to be an open earthen channel with no controls preventing the subsurface seepage of mobile DNAPL into the stream.
- DNAPL that potentially enters the stream in these areas, can travel through the DS Tributary culvert (i.e. through a known opening within the slurry wall) and then

- accumulate in sediments west of State Rd, where pooled DNAPL has remained since its discovery in 2005.
- DNAPL that pools in the streambed west of State Road may then percolate downward through sediments/soils to the North Sewer and other similar preferential pathways (CEI conduit, waterline), described in further detail below.

Overall, once Detrex DNAPL enters the upstream (unprotected) portion of the DS Tributary, DNAPL can migrate downstream, across the slurry wall and west of State Road. Once west of State Road, there are no controls to prevent downward percolation of DNAPL to underground utilities or continued transport through the DS Tributary to Fields Brook. In addition, to the best of our knowledge, the integrity of the piped section of DS Tributary and the effectiveness of the "passive" groundwater collection trench present in this area have never been assessed. Consequently, DNAPL in the piped section of the DS Tributary could also be leaking through and entering the subsurface.

Pathway 2 – Underground Utilities

Underground utilities (the North Sewer, CEI conduit, and water line) serve as preferential conduits between DNAPL source areas on the Detrex property (described below) and Fields Brook. Soil concentrations indicative of mobile DNAPL and/or liquid DNAPL has been observed near/ within each of these utilities. There are at least three potential sources of DNAPL to these conduits:

- DNAPL seeps observed in the DS Tributary sediments west of State Road are a potential source of DNAPL to underlying utilities, especially the North Sewer, which directly underlies the DS Tributary culvert outfall (Figure 3). The cross-section along the North Sewer (Figure 3) shows evidence of downward DNAPL migration, with concentrations indicative of mobile DNAPL extending from the DS Tributary sediments down to the North Sewer and water line.
 - Given that contaminated groundwater (18,000 gallons, super-saturated with Detrex DNAPL compounds) flowed out of the North Sewer area during the State Road Bridge construction work and an opening on the top of the pipe showed that the North Sewer was filled with water (Figure 6), it is evident that groundwater infiltrates through cracks/holes in the pipe and then migrates towards Fields Brook. Given the proximity of the North Sewer to upgradient DNAPL findings (Figure 3), this pipe clearly is facilitating the transport of DNAPL and contaminated groundwater.
- The abandoned Detrex outfall, which potentially bypasses the slurry wall on the Detrex property, historically discharged into the North Sewer (Figure 4). In cross-section view (Figure 4), several C_{mobile} exceedances coincide with the depth of the former Detrex outfall. Because the groundwater interceptor trench operates passively and the abandoned outfall is below the trench, DNAPL that migrates along this conduit will not be captured by the trench. Additionally, since it is unknown whether the former Detrex outfall at the North Sewer junction was sealed as part of the abandonment process (no seal is shown on the North Sewer abandonment as-built drawings), this pipe potentially provides an ongoing migration mechanism from the Detrex source area to the North Sewer and other underground utilities below the outfall.
- The observation of DNAPL within the excavation during the slurry wall installation and detection of soil concentrations indicative of mobile DNAPL in recent borings (e.g.,

DPT-13, DPT-20; Figure 4) indicate that mobile DNAPL is present on the Detrex property between the slurry wall and State Road. The CEI conduit and water line underlie this area and are potential receptors for downward migrating DNAPL (Figure 3). Similar to the North Sewer, these utility lines slope towards Fields Brook and serve as DNAPL migration conduits, as evident from DNAPL seeps observed emanating from these lines at Fields Brook when the State Road Bridge work was being undertaken (see Figure 7 and Attachment 2).

Pathway 3 – Geological Features

As described in previous memoranda (e.g., Gradient, 2008), natural geological features (e.g. clay and till surfaces, fractures, and sand seams) function as preferential DNAPL migration pathways at the Site. The lacustrine clay surface map that was developed for the Detrex property and adjoining areas clearly indicates that the former Detrex process lagoon area, where a substantial volume of DNAPL is still present, is located at a topographic high, with the clay surface sloping downward towards the south, west, and southwest (Figure 8). In addition, the clay surface contours reveal the presence of distinct troughs or valleys, southwest of the Detrex process lagoons (Figure 8). These troughs serve as natural areas for DNAPL collection and migration – a conclusion corroborated by the presence of DNAPL in 2005 at a number of locations aligned with these troughs (Figure 8). The pooled DNAPL in the lagoon area provides the necessary fluid pressure or "driving head" to allow for continuous DNAPL migration along the surface of the lacustrine clay and via sand lenses and fractures within the lacustrine clay. This is evident from the observation of DNAPL pooling on the surface of the clay and seeping from sand seams during the State Road Bridge replacement work, and other sampling and construction activities at the Site.

Thus, although the DS Tributary and underground utilities are significant preferential DNAPL migration pathways and pose the greatest ongoing threat to EU6, DNAPL transport *via* sand seams/ clay fractures are critical elements that facilitate DNAPL migration at the Site.

The various preferential pathways described above provide a logical set of DNAPL migration mechanisms that explain the repeated findings of C_{mobile} exceedances and DNAPL seeps throughout the Detrex property, along the DS Tributary and in Fields Brook. These pathways also illustrate that there are gaps and holes in the Detrex source control remedies that allow DNAPL to migrate from the former lagoon area to Fields Brook, in particular the EU6 section of the brook. Furthermore, this emphasizes the need for Detrex to fully define and urgently address DNAPL migration through these preferential pathways, a conclusion and recommendation also reached by EPA during the 5-year remedy review (US EPA, 2009):

"Although complete removal of DNAPL is not possible, DNAPL is considered a principal threat at the Detrex operable unit and its presence at the site may present a risk to Fields Brook. For this reason, additional work is necessary to address operational difficulties with the existing extraction wells by expanding the DNAPL extraction system to achieve broader DNAPL removal. In addition, the continued assessment of the contamination seen in the DS Tributary, just west of State Road, may ultimately lead to a reassessment of the short-term protectiveness of the remedy. If investigations indicate that the DNAPL in the DS Tributary is due to a failure of the existing DNAPL control measures, additional work will be required to correct the situation (pg. 27)."

5 Conclusions

The following conclusions are based on a comprehensive review of the source control remedy implemented by Detrex and environmental data collected at the Detrex facility and downgradient areas:

- The improper design and poor operation and maintenance practices of the Detrex source control measures have resulted in the removal of only a small volume of the DNAPL present in the former lagoons. The large volume of DNAPL that remains in the source area provides the driving head for outward migration towards the southern, western and northwestern portions of the Detrex facility and beyond.
- The migration of DNAPL beyond the source area at the Detrex facility is ongoing due to the poor implementation of migration control elements of the Detrex remedy.
 - Segments of the slurry wall that were intended to prevent migration to the northwest and southwest of the source area were not installed and the overall length of wall was less than one third of the anticipated length in the ROD. In fact, the slurry wall appears not to have been installed beyond the leading edge of the DNAPL plume, as required by the ROD.
 - The passive groundwater collection trenches installed in lieu of the active extraction well system envisioned by the ROD is less effective than an active system at inducing an inward hydraulic gradient upgradient of the slurry wall and cannot capture DNAPL that lies beneath the trench. Due to a lack of performance data, the effectiveness of the passive system cannot be evaluated.
 - Although sections of the DS Tributary were placed in a pipe, the upstream sections of the stream appear to have been left uncontained. In addition, no performance monitoring data has been collected to evaluate whether piping of DS Tributary has adequately eliminated DNAPL seepage (e.g., through pipe joints) or to evaluate whether any DNAPL is entering the stream in the uncontained section of the stream.

The failure of these remedial measures to effectively mitigate DNAPL migration has resulted in deteriorating conditions in the DS Tributary and Fields Brook. This is especially evident from the recent and repeated observation of DNAPL seeps in sections of the DS Tributary and Fields Brook where DNAPL was not identified during the 2001 remediation efforts or pre-remediation investigations.

- The widespread exceedances of C_{mobile} (an indicator of the presence of mobile DNAPL in a fractured clay system) on the Detrex facility, beneath the groundwater interceptor trench (upgradient of the slurry wall), and west (downgradient) of the slurry wall demonstrate the presence of mobile DNAPL over a large area (up to over 600 feet away) downgradient of the former Detrex lagoons.
- The distribution of C_{mobile} exceedances and DNAPL seeps reveal that DNAPL migration towards Fields Brook occurs primarily via the DS Tributary and underground utilities that run parallel to State Road:
 - Soil concentrations indicative of mobile DNAPL are present on both sides of the "uncontained" section of the DS Tributary on the Detrex facility. DNAPL could be entering the DS Tributary in these sections and possibly along joints in the

culverted section of the stream. Once such DNAPL enters the DS Tributary, it can readily flow west *via* the culvert (that runs *through* the slurry wall) and discharge into stream sediments, west of State Road, a location where DNAPL has been observed.

• The DS Tributary and elevated soil/sediment concentrations overlie utilities (e.g. the North Sewer, CEI conduit, and water line) and mobile DNAPL from such sources could readily enter utilities and migrate *via* gravity towards Fields Brook.

Overall, migration of DNAPL via these preferential pathways, which are fed by DNAPL migration along geologic features (e.g., sand seams, clay fractures in the lacustrine clay) from the source area continue to threaten the EU6 portion of Fields Brook. Immediate action is necessary to address/eliminate these preferential migration pathways and to undertake more aggressive measures to remediate the DNAPL source area.

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Tables

Tables Gradient

Table 1
DS Tributary Sediment Sampling just West of State Road (November 2008)
Fields Brook Superfund Site, Ashtabula, Ohio

Sample ID Compounds	RAL (mg/kg)	C _{sat} (mg/kg)	DS-SD09	DS-SD10	DS-SD11	DS-SD12	DS-SD13	DS-SD13 (Duplicate)
VOCs (mg/kg)								
1,2-Dichloroethene (Total)		2.3	2.4	ND	220	29	36	6.9
Trichloroethene	1,854	139	4.3	ND	28	7.2	120	49
Tetrachloroethene	392	2.8	0.88	ND	120	6	170	110
1,1,2,2-Tetrachloroethane	102	223	0.92	ND	22	4.8	18	12
Total Chlorinated VOCs *			8.5	ND	390	47	344	178
SVOCs (mgkg)								
Hexachlorobutadiene		1.0	27	8.6	190	18	620	220
Hexachlorobenzene	39	0.003	33	19	120	34	ND	130
PCBs (mg/kg)								
Total PCBs	6.4		ND	ND	ND	ND	ND	ND

Notes.

Data in italics indicate RAL exceedances.

Data in bold red indicate C_{sat} exceedances.

ND - Non-detect.

^{* -} Only the select VOCs listed above were included in the Total Chlorinated VOC calculation.

Table 2
Summary of Frac Tank Water Sampling Results: State Road Bridge Expansion
Fields Brook Superfund Site, Ashtabula, Ohio

		Frac Tank Water Samples (mg/L)							
Compound	Calculated Effective Solubility (mg/L) 1	North Sewer Seepage (18,000 gallons; 1/5/09)		North Footer (18,000 gallons		CEI Conduit Seepage (10,000 gallons; 1/19/09)			
		Concentration	Ratio ²	Concentration	Ratio ²	Concentration	Ratio ²		
1,1,2-Trichloroethane	0.29	0.36	122%	0.12	41%	ND	NA		
1,2-Dichlorobenzene	0.056	0.090	161%	0.012	22%	ND	NA		
Chloroform	11	ND	NA	ND	NA	ND	NA		
Tetrachloroethene	13	34	255%	11	83%	3.2	24%		
Trichloroethene	673	44	7%	30	4%	9.1	1%		
1,2-Dichloroethene (total)	11	1.4	12%	4.4	39%	1.6	14%		
1,1-Dichloroethene	2.9	0.29	10%	0.43	15%	0.12	4%		
1,1,2,2-tetrachloroethane	1060	0.33	0.03%	0.51	0.05%	0.20	0.02%		
Hexachloroethane	1.0	0.26	26%	0.0056	1%	0.0066	1%		
Hexachlorobutadiene	0.025	0.069	278%	0.010	39%	0.0039	16%		
Hexachlorobenzene	2.39E-05	ND	NA	ND	NA	ND	NA		
4-chloro-3-methylphenol	6.1	ND	NA	ND	NA	ND	NA		

Note:

ND - Not Detected.

NA - Not Available

Data in bold red indicate that the concentration exceeds 1% of the calculated effective solubility limit.

J - Lab estimated value.

 $^{1 - \}textit{Effective Solubility (using MW-07S DNAPL sample)} = \textit{Solubility Limit } x \textit{ Initial Mole Fraction}.$

^{2 -} Ratio: (Measured concentration/Effective Solubitility) * 100.

Table 3
Summary of Soil Pile Sampling Results: State Road Bridge Expansion
Fields Brook Superfund Site, Ashtabula, Ohio

Compound		Pile A - North Sewer Interceptor Trench/ North Footer 1/13/2009	Pile B - Seep on East Side of State Road 1/13/2009	Pile C - North Footer 1/20/2009	Pile D - CEI Vault Sump 1/20/2009	C _{sat} (mg/kg)
VOCs	(units are in mg/kg)					
	Cis-1,2-Dichloroethene	1.8	4.2	10	2.0	2.3
	1,1,2,2-Tetrachloroethane	ND	3.8	ND	ND	334
	Tetrachloroethene	200	150	180	91	5.1
	Trichloroethene	150	64	97	63	186
	Total Chlorinated VOCs *	352	222	287	156	
SVOCs	(units are in mg/kg)			_		
	Hexachlorobenzene	1.1	1.5	0.76	0.68	0.04
	Hexachlorobutadiene	2.1	2.3	1.0	1.3	6.81
	Hexachloroethane	0.6	ND	ND	ND	

Note:

ND - Not Detected.

Blank Cells - Sample not analyzed for the compound.

J - Lab estimated value.

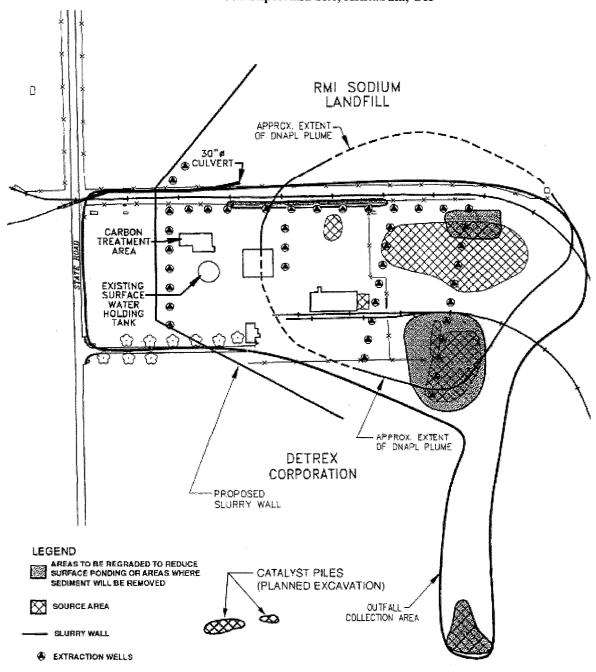
^{*} Only select VOCs (cis-1,2-Dichloroethene, Trichloroethene, Tetrachloroethene and 1,1,2,2-Tetrachloroethane) were included in the Total Chlorinated VOC calculations.

⁻ Data in bold red indicate that the soil concentration exceeds the soil saturation (C_{sat}) value. Soil C_{sat} values were calculated only for the main Detrex marker compounds.

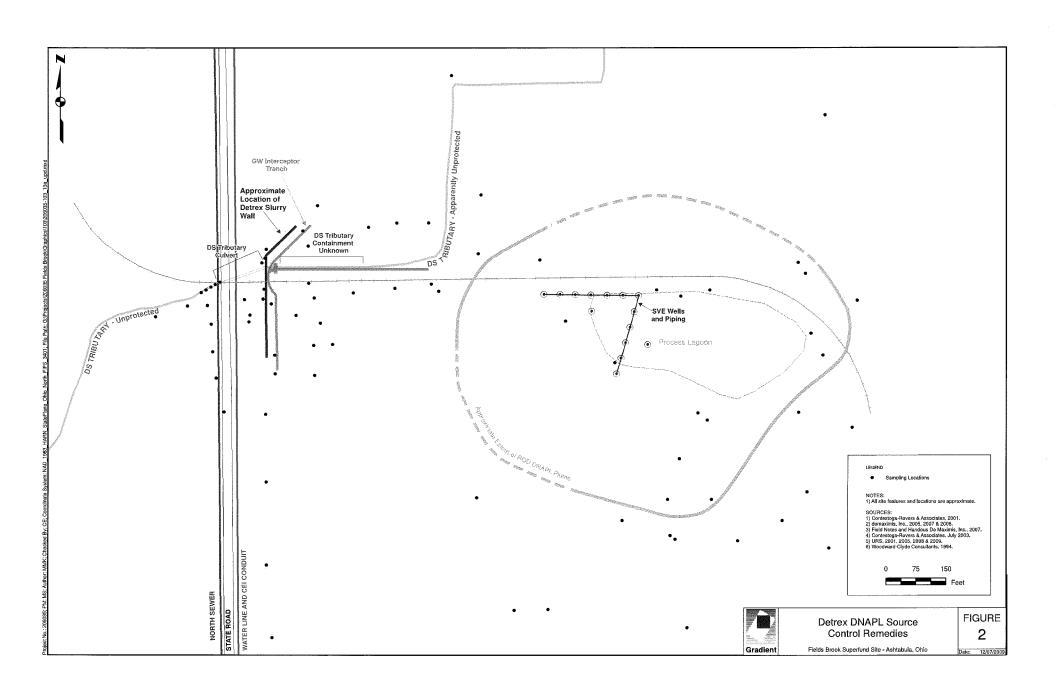
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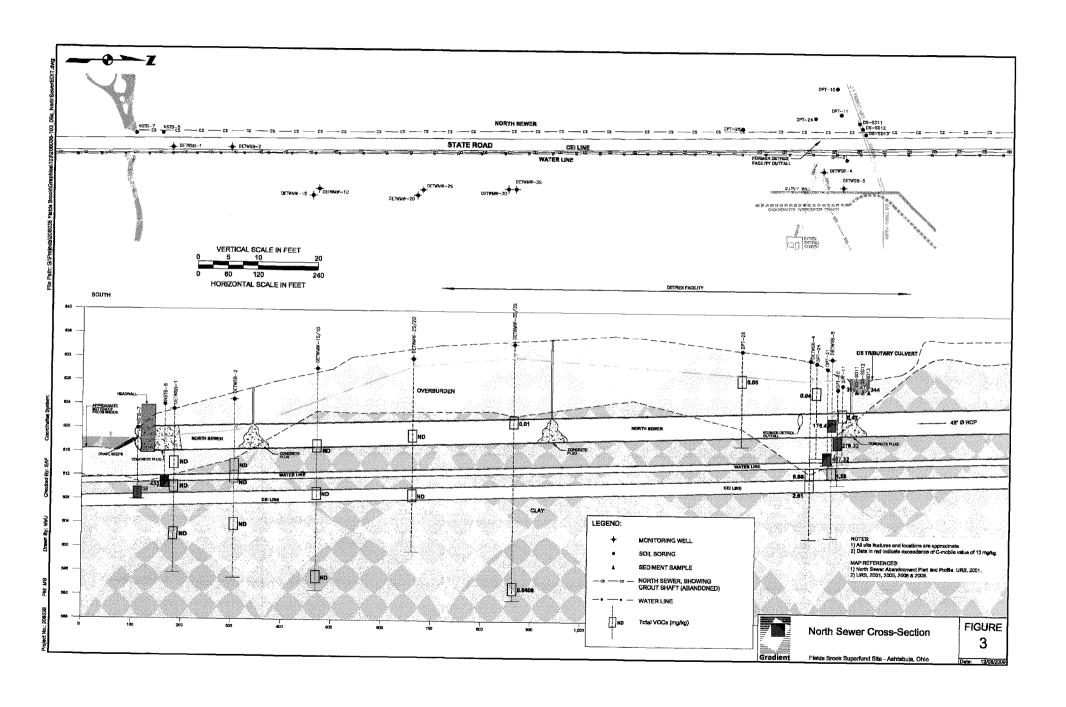
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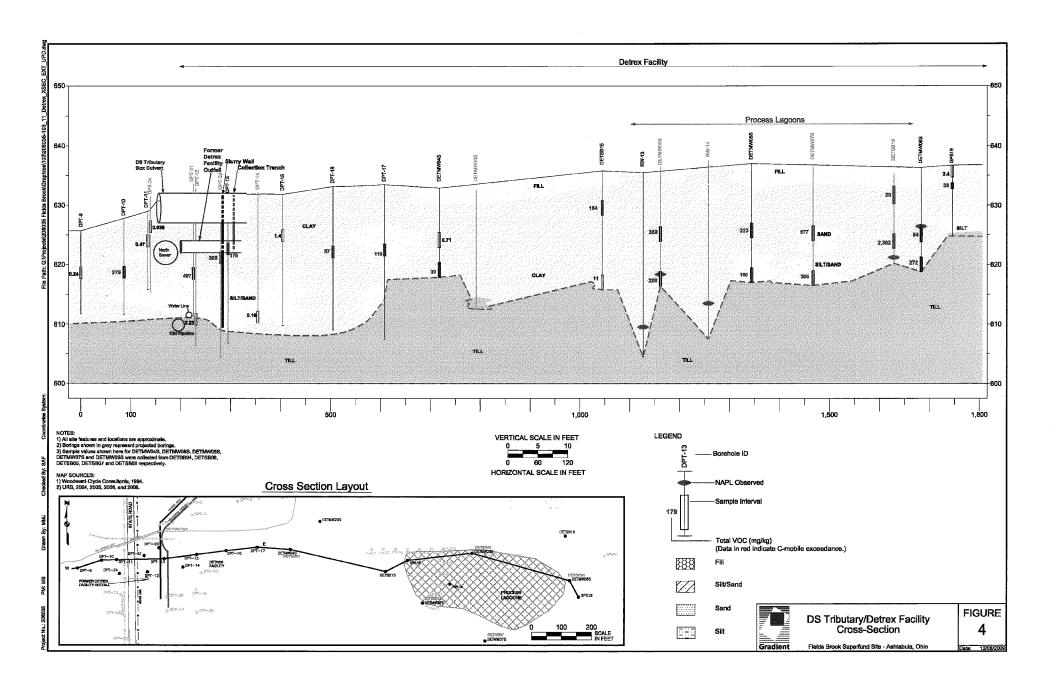
Figure 1
Extent of the Detrex DNAPL Plume (Figure 7 from the SCOU ROD)
Fields Brook Superfund Site, Ashtabula, OH

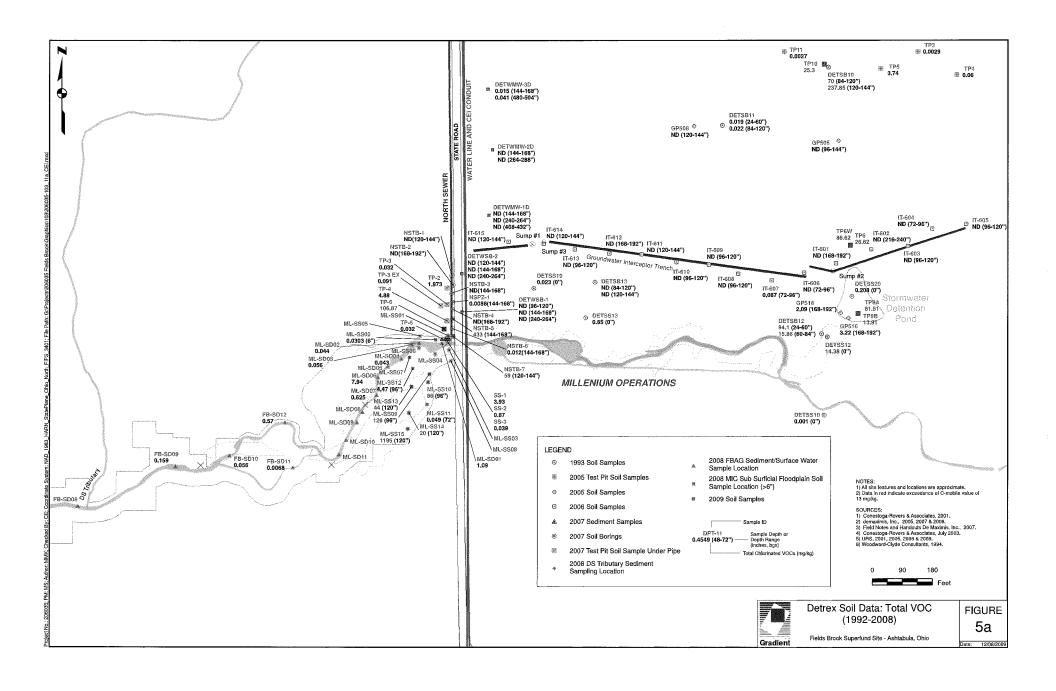


DETREX Site Map









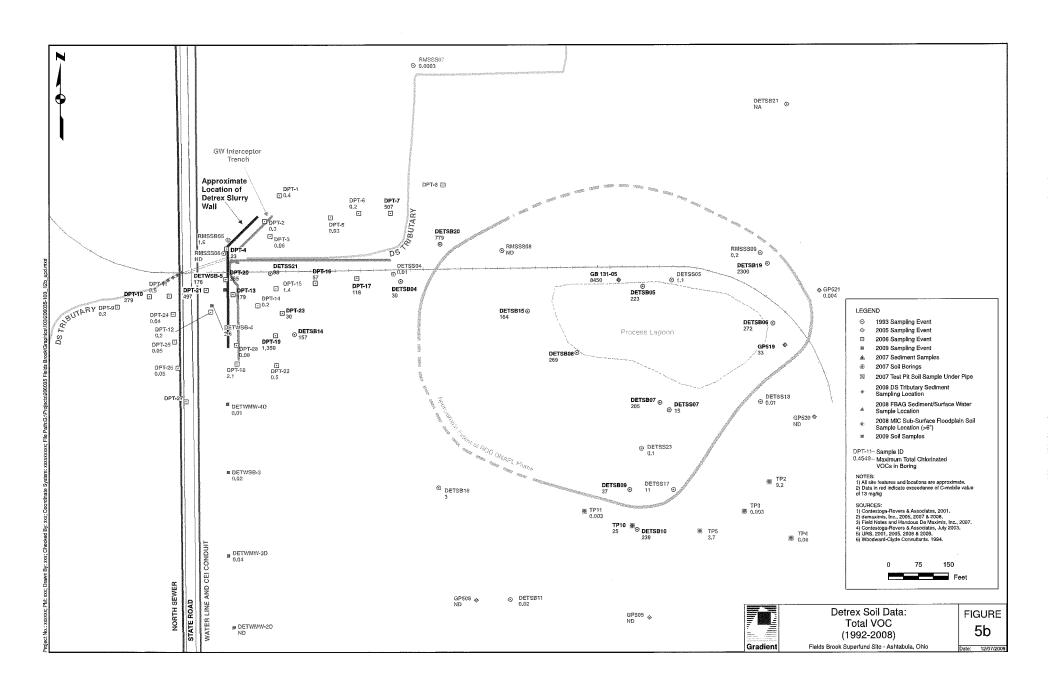
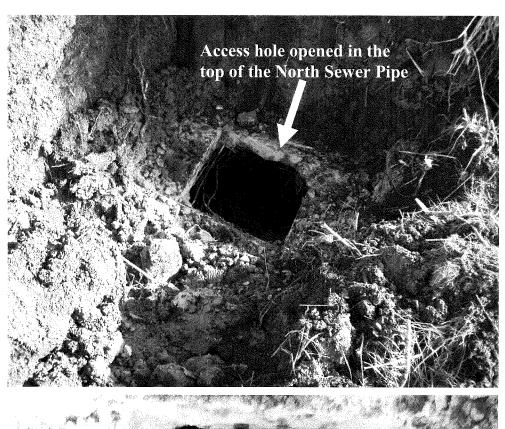


Figure 6
Photos of the North Sewer Filled with Water



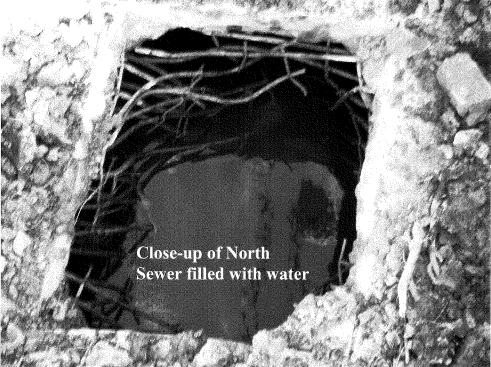
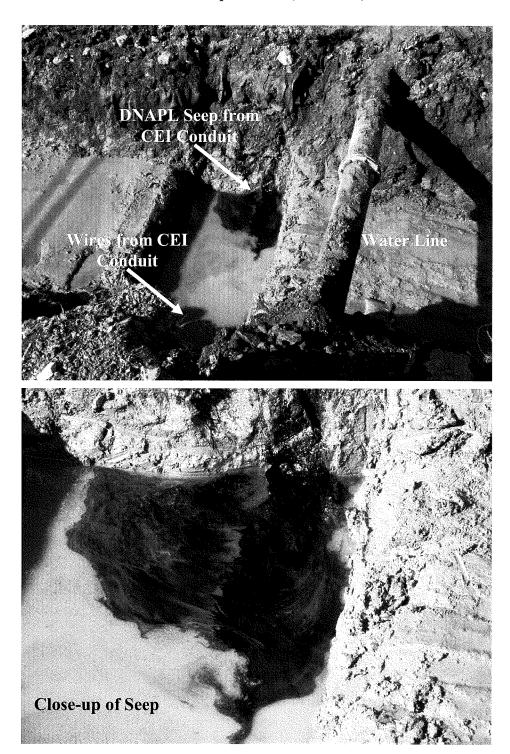
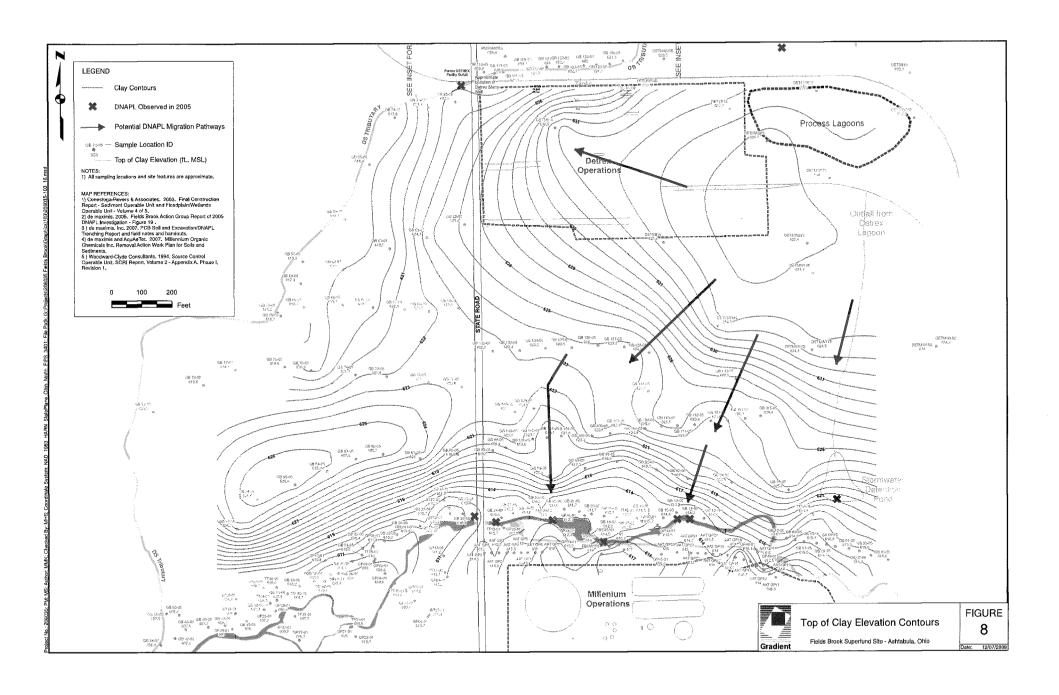


Figure 7
Detrex DNAPL Seep from the CEI Conduit
Fields Brook Superfund Site, Ashtabula, OH





Attachment 1

Attachment 1 Gradient



July 15, 2009

Leah Evison, Ph.D. U.S. EPA Region 5 77 W. Jackson Blvd. Chicago, IL 60604-3507

Subject:

Detrex's Proposed Source Control Enhancements Fields Brook Superfund Site, Ashtabula, Ohio

Dear Leah:

Gradient and FBAG have reviewed Detrex's proposed Source Control enhancement proposal¹ and other related documents. 2,3 The Detrex Source Control enhancement proposal is inadequate relative to the scale of the DNAPL problem and will not accelerate DNAPL removal rates, a critical and urgent performance criterion for effective source control. Until mobile DNAPL is reduced to residual state, it will continue to migrate in multiple directions from the source zone and impact Fields Brook and the completed remedial actions. The current Detrex pilot system suffers from several design deficiencies and is operated sub-optimally by Detrex. Consequently, DNAPL thicknesses within the limited area influenced by the pilot system have not declined in over 6 years of operation. On the order of 10 feet of DNAPL continually accumulates in wells (see attached Figure 1) despite over 15,000 gallons of DNAPL having been removed. This is clear evidence that DNAPL in the source area is mobile. Given the limited spatial coverage of the current system, the vast majority of DNAPL that is present at the Detrex facility migrates *via* multiple subsurface preferential pathways (*e.g.*, clay fractures, utilities such as the CEI conduit and the North Sewer) away from the pilot system. Detrex needs to take aggressive source remediation steps now to address this serious issue.

1. The current Detrex Source Control system is under-sized, poorly designed, and does not utilize EPA-recommendations/Best Practices for Soil Vapor Extraction/Dual Phase Extraction (SVE/DPE) systems.

The current Detrex SVE/DPE system is a small pilot unit installed in October 2002 that which was never "scaled-up." The system consists of 12 two-inch diameter extraction wells, which affect only a small fraction of the 500,000 square foot DNAPL source area (note, the 1997 ROD design called for 40 wells). In addition, the system design does not conform to best practices set forth in EPA guidance⁴ for SVE/DPE systems and has the following major deficiencies:

¹ URS Corporation. 2008. Interim Operations and Maintenance Manual, Detrex RD/RA Source Control Area – Detrex Facility, Ashtabula, Ohio. June 2008.

² URS Corporation. 2004. Operation & Maintenance Manual, Source Control & Vacuum-Enhanced DNAPL Recovery System – Detrex Facility, Ashtabula, Ohio. March 2004.

³ Detrex Corporation. 2009. Monthly Status Report – April 2009, Fields Brook Superfund Site, Detrex Source Area, Ashtabula, Ohio. May 14, 2009.

⁴ US EPA. 2004. How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites – A Guide for Corrective Action Plan Reviewers. Office of Solid Waste and Emergency Response. EPA 510-R-04-002. May 2004.

- The current SVE/DPE well configuration (a V-like shape) does not provide adequate spatial coverage over the DNAPL footprint to efficiently remove contaminants. In low permeability soils, the radius of influence associated with a SVE/DPE well is small, thereby requiring a closely spaced network of wells. Typically, spacing of SVE/DPE wells is defined on the basis of radius of influence data collected during a pilot test. It is not clear that such information has been collected at the site. Absent such site-specific data and using a typical radius of influence of 5 feet for fine grained soils (USEPA, 2004), the current system covers less than 1% of the 500,000 square feet DNAPL plume defined in the 1997 ROD. Even if the site-specific radii of influence were somewhat higher, the current system's spatial coverage is extremely small given the extent of contamination.
- The vacuum SVE/DPE blower being utilized is inappropriate for the site's subsurface conditions. In low permeability silt/clay soils found at the Detrex facility, a high-vacuum blower (rotary lobe or liquid ring) is needed to effectively extract contaminant mass (USEPA, 2004). However, the Detrex system utilizes a midrange vacuum pump that is not appropriate for the site, resulting in sub-optimal contaminant removal rates.
- The small diameter (2-inches) of the SVE/DPE wells limits the operational efficiency of the system and greatly limits operational flexibility. For example, if the wells were 4-inch in diameter, a submersible water withdrawal pump could be placed in the well to simultaneous remove DNAPL and groundwater, while the vacuum pump extracts vapors a proven approach known as Vacuum Enhanced Pumping (VEP).
- Finally, air injection wells are often required in low permeability soils/strata to provide the necessary air flow and to prevent short-circuiting of extraction wells (USEPA, 2004). Such wells have not been installed.

2. The Detrex Remedy is not being operated efficiently and the operational problems are a manifestation of the poor design.

Although the SVE/DPE wells have an approximately 15 feet long well screen, only the lower 1 to 2 feet is "open," with the remainder having been blocked off using a solid riser. This design modification and the manner in which the system is being operated (*i.e.*, only during business hours) are key elements contributing to the poor perceived system performance.

- Since a majority of the SVE/DPE well screen is blocked off and groundwater and DNAPL (total liquid thickness of approximately 15 feet) accumulates in the wells, it does not appear that any air flow is induced in the subsurface by vacuum application.⁵ Therefore, the current system is largely removing liquids and very limited vapors an extremely inefficient approach for remediating a VOC-dominant DNAPL that is best remediated by vapor removal.
- Detrex's decision to operate the system manually, only during business hours, is extremely inefficient and inexplicable. The intermittent operation of the system allows groundwater to flow back into wells when the system is not operating a

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⁵ We could not find any air flow rate or VOC vapor removal rate data in the Detrex documents (*e.g.*, in the O&M report). Such data are critical for understanding system performance and is typically presented in O&M reports.

less than ideal scenario. For effective contaminant mass removal in this setting, the sub-surface needs to be dewatered by continuous groundwater extraction, in conjunction with vapor flow induced by vacuum application.

• The remedy system O&M difficulties reported by Detrex (e.g., well siltation) is a symptom of poor system design and operation. These O&M difficulties could be caused by the poor choice of vacuum blower and inappropriate sizing of the well's filter pack. DPE/SVE is a proven technology and has been effectively applied at numerous sites around the country in similar low permeability settings. Therefore, the operational difficulties are a design, and not a technology efficacy issue.

3. Despite the system's limitations, it continues to recover DNAPL mass – an indication of the volume of DNAPL present in the sub-surface.

The system has recovered 15,680 gallons of DNAPL as of April 2009, a remarkably large volume, given the limited scale of the system and the inefficient manner in which it is being operated. However, DNAPL thicknesses have not declined appreciably since system operations began and DNAPL continues to flow into the wells (Figure 1). These findings are important for two reasons:

- First, continued DNAPL accumulation in wells is clear, indisputable indication of its subsurface mobility. Furthermore, DNAPL migration into the pilot system's area of influence, only a small fraction of the larger plume area, causes major concern over the fate of the mobile DNAPL beyond the area of influence of the extraction wells.
- Second, the collection of this volume of DNAPL in a poorly designed, sub-optimally operated pilot-scale system is clear indication of the vast DNAPL reservoir (previously estimated to be at least 250,000 gallons) that remains at the Detrex facility. In addition, these DNAPL recovery data demonstrate that much higher DNAPL recovery, a critical component of effective source control, can be achieved at the Detrex site using a properly designed, installed and operated system.

4. The proposed system enhancements are inadequate; Detrex needs to take more aggressive steps to enhance DNAPL and contaminant mass recovery.

Detrex proposes a gravity-drain system consisting of a line of wells or a collection trench along a portion of the northern Detrex property boundary. Accumulated DNAPL will be pumped out monthly. This proposed system is technically ineffective and spatially deficient because:

- The proposed "enhancements" are "passive" systems (monthly DNAPL removal) similar to the current Detrex system, which is being operated manually at an unknown frequency. Consequently, the enhancement will likely further reduce DNAPL removal rates, not increase them.
- The focus on a limited area to the north of the source area is perplexing in that it does not focus on identified preferential pathways (e.g. CEI conduit and the North Sewer) that require immediate action to prevent continued impacts to Fields Brook.

What is needed is an aggressive system that actively targets and removes DNAPL and VOC mass from the sub-surface. The system needs to be designed to achieve the critical source control

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objective of reducing DNAPL to a residual, non-mobile state, and to do so in a timely manner. This means that it not only needs to be properly designed, but also correctly located spatially and effectively operated until the design objectives are achieved. USEPA (2004) clearly states that an SVE/DPE system will recover more DNAPL overall and at a faster rate than a gravity drain system⁶.

Finally, a properly designed and implemented SVE/DPE system is an essential building block for remediating such a site and can later be augmented by more aggressive in-situ thermal treatment technologies (e.g., steam injection, six-phase heating, etc.). The scientific literature is replete with case studies of successful application of SVE/DPE-based applications in geologic formations and under similar conditions to that at Detrex's property.^{7,8} It has been done elsewhere and urgently needs to be done here.

Overall, Gradient and FBAG believe that Detrex needs to implement more effective source remediation measures immediately at their property. We would be happy to further discuss our thoughts on this topic at your convenience.

Please feel free to call me if you have questions or would like to discuss this further.

Yours truly,

GRADIENT CORPORATION

Manu Sharma, P.E.

Principal

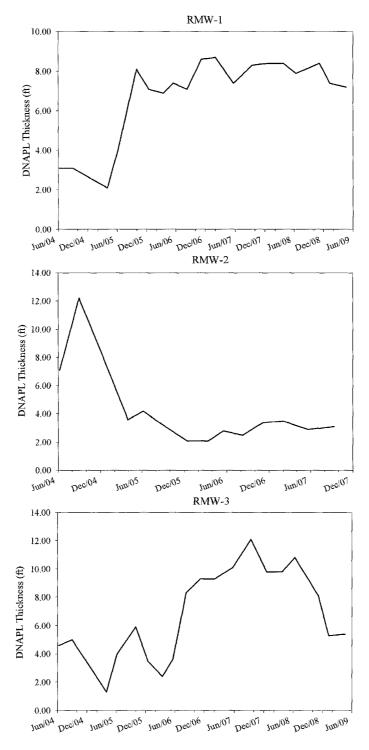
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⁶ US EPA. 2004. How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites – A Guide for Corrective Action Plan Reviewers. Office of Solid Waste and Emergency Response. EPA 510-R-04-002. May 2004.

⁷ US EPA. 2004. In-situ Thermal Treatment of Chlorinated Solvents: Fundamentals and Field Applications. Office of Solid Waste and Emergency Response. EPA/542-R-04-010. March 2004.

⁸ US EPA. 2000. Dense Non-Aqueous Phase Liquids (DNAPLs): Review of Emerging Characterization and Remediation Technologies. Interstate Technology and Regulatory Council (ITRC). June 2000.

Figure 1
DNAPL Thicknesses Observed in Detrex Source Control Monitoring Wells
Detrex Facility, Fields Brook Superfund Site, Ashtabula, OH



Source: Detrex Corporation. 2009. Monthly Status Report – April 2009, Fields Brook Superfund Site, Detrex Source Area, Ashtabula, Ohio. May 14, 2009.

Attachment 2

Attachment 2 Gradient

STATE RD BRIDGE: SOUTH SECTOR PRODUCT REMOVAL

WATERLINE AND SE SEWER

By volume, the area beneath and adjacent to the trunk waterline, and beneath the 24 inch SE Sewer, yielded the most free product. The gravel bedding and urban fill appear to have been a preferential pathway as evidenced by the ubiquitous presence of product, while in contrast, product generally terminated at fill interface with native soils, except where sand seams were present. A product containing sand seam was found 3 ft below and 4 ft East of the SE sewer, at roughly the same elevation as the Waterline. The area beneath and East of the Sewer is a mixture of urban fill containing, gravel, brick, wood and assorted stone. Product was pervasive in this material. The 24inch sewer is located 24 ft East of the centerline of State Rd.

Estimated Product Volume: ½ gallon (typically in soil matrix – no large free pools)

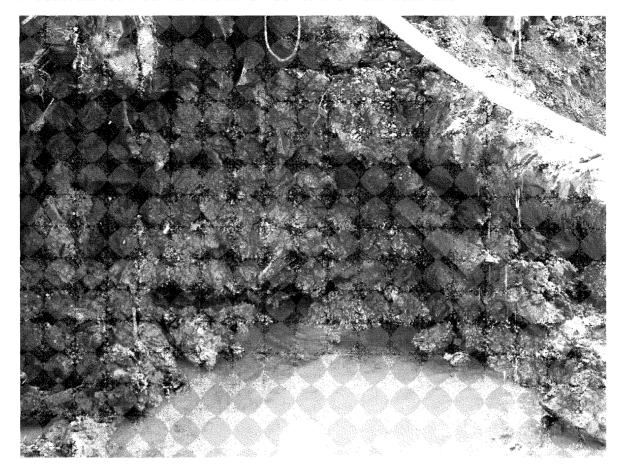
Depth: 12-13ft below ground surface (BGS) or Gradient G – G' Cross Section: 611-612 Elevation (Aprox.)

Lithology: Interface of Clayey Silt/Lacustrine Clay

Tech is standing on Trunk Water line and looking South at 24" Sewer



Product stained urban fill beneath SE Sewer and Trunk water line



BRIDGE FOOTERS

Bridge Footers were impacted along the entire length of the South Sector. Product stained concrete and soils in vicinity were removed and accounted for bulk of soil removal.

Estimated Product Volume: Difficult to determine volume (typically in soil matrix)

Depth: 13-14ft below ground surface (BGS) or Gradient G – G' Cross Section: 610-609

Elevation (Aprox.)

Lithology: Lacustrine Clay and Silty Clay interface (Lacustrine Dominant)

SMALL VOLUME PRODUCT FIND 1

On 3/3/09, an estimated 1 ounce of DNAPL product was encountered at approximately 12 ft BGS near centerline of State Rd. Product appeared isolated and did not require extensive removal activity.

Estimated Product Volume: 1 ounce (with soil matrix)

Depth: 12ft below ground surface (BGS) or Gradient G – G' Cross Section: 612

Elevation (Aprox.)

Lithology: Lacustrine Clay and Silty Clay interface

SMALL VOLUME PRODUCT FIND 2

On 3/3/09, an estimated ½ to 1 ounce of DNAPL product was encountered at approximately 12 ft BGS and was 20 ft West of centerline of State Rd (near gasline). Product appeared isolated and did not require extensive removal activity.

Estimated Product Volume: <1 ounce (with soil matrix)

Depth: 12ft below ground surface (BGS) or Gradient G – G' Cross Section: 612 Elevation (Aprox.)

Lithology: Lacustrine Clay and Silty Clay interface

Additionally:

The North Side appears to mirror the South in that the footers were impacted at similar elevation as the South Footers and that copious Free Product finds were most often associated with urban fill around utility structures such as waterlines and sewers. The fill chosen by builders of the original bridge was construction rubble mixed with clayey silty soils including: brick, stone, slag, gravel and wood.

The North Sewer and the area in and around the Waterline yielded the greatest product volumes. North Sewer produced the greatest volume: soil matrix with 1/2 gallon to a gallon of product.

North Section of Waterline produced a similar volume as the South Section (aprox. 1/2 gal) in the same basic bedding plain and materials:

Depth: 12-13ft below ground surface (BGS) or Gradient G – G' Cross Section: 611-612

Elevation (Aprox.)

Lithology: Interface of Clayey Silt/Lacustrine Clay

The sand seam in F-F' was not prevalent under the bridge (that we could see).

Attachment 3

Attachment 3 Gradient

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de maximis, inc.

3148-A Southgate Circle Sarasota, FL 34239 (813) 365-8444 Fax (813) 365-8929

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OSC MILLER / IRWIN

01/04/96

OSC MILLER RECEIVED CALL FROM AL GEPHART OF CENTERIOR ENERGY. AL REPORTED THAT THERE IS A CENTERIOR POWER CABLE RUN ALONG STATE ROAD, NORTH OF 21 ST STREET BY THE RAILROAD TRACKS. A MAINTENANCE CREW WAS TRYING TO REPLACE A FAULTY POWER CABLE AND HAD TO PLACE WORKERS INTO AN UNDERGROUND CABLE VAULT. THE CABLE VAULT WAS FOUND TO BE CONTAMINATED WITH WHAT CENTERIOR BELIEVES TO BE A CHLORINATED HYDROCARBON (VERIFIED BY LABORATORY ANALYSIS). CENTERIOR ATTEMPTED TO PUMP THE CHEMICAL CONTAMINATED WATER OUT OF THE VAULT; BUT CEASED PUMPING WHEN POLLUTANT CONTINUED TO ENTER VAULT FROM SURROUNDING AREA.

OSC IRWIN IDENTIFIED THIS LOCATION AS WITHIN OR ADJACENT TO THE "FIELDS BROOK SUPERFUND SITE" LOCATION. CONVERSATIONS WITH DERRRS STAFF WOULD INDICATE THAT THE CHEMICAL CONTAMINATION IN THE CABLE VAULT IS LIKELY TO BE FROM THE SUPERFUND SITE, MORE SPECIFICALLY, DETREX CHEMICAL COMPANY. ONE RRS STAFF MEMBER MADE THE STATEMENT THAT SHALLOW GROUNDWATER MONITOR WELLS ON DETREX PROPERTY WERE FOUND TO HAVE OVER 30" OF FREE-PHASE CHLORINATED SOLVENT CONTAMINATION.

ALTHOUGH PRIMARILY AN DERR-RRS ISSUE, DERR-RR WOULD LIKE TO DETERMINE IF ANY FREE-PHASE GROUNDWATER CONTAMINATION IS ACTIVELY DISCHARGING TO STORM SEWERS AND/OR SURFACE WATERS. ALSO, IF THE CONTAMINATION OF THE CABLE VAULT DOES INDEED APPEAR TO BE RELATED TO THE SUPERFUND SITE.

IF DERR-ER DETERMINES THAT THERE IS NO ENVIRONMENTAL EMERGENCY CONDITIONS IN OR AROUND THE CABLE VAULT AND THE PROBLEM APPEARS TO BE RELATED TO THE SUPERFUND SITE, DERR-ER WILL BE REFERRING THE INCIDENT TO DERR-RRS FOR FOLLOW-UP INVESTIGATION.

FIELDS BROOK SUPERFUND SITE - OPPA CONTACT: REGAN WILLIAMS - USEPA CONTACT: ED HAMLIN

Attachment 4

Memorandum



To: FBAG Technical Committee

Date: December 9, 2008

From:

Manu Sharma

Subject:

Detrex DNAPL Analysis

The FBAG Technical Committee asked that we present and analyze data that have been collected at the Detrex groundwater interceptor trench (southern edge of Detrex property), the North Sewer, and the DS Tributary (western edge of Detrex property) to assess whether DNAPL is continuing to migrate from the former Detrex Lagoons. We understand that USEPA has requested FBAG to provide them with the calculations, analysis and underlying data that underscores FBAG's assertion that Detrex DNAPL is not confined to the northeast and north central portion of the Detrex facility, is present at multiple locations adjacent to the facility, and is moving towards and entering Fields Brook. In particular, the analysis results demonstrate the following:

- 1. Detrex DNAPL is migrating into the Detrex groundwater interceptor material that was migrating into the EU8 portion of Fields Brook prior to trench installation in January 2007 (to the south);
- 2. DNAPL has migrated beyond the Detrex slurry wall and is manifesting itself at the DS tributary (to the west); and
- 3. DNAPL has migrated beyond the western boundary of the Detrex facility and is manifesting itself along the North Sewer and eventually entering Fields Brook in EU6 (to the southwest).

In summary, source control measures undertaken at Detrex have been inadequate, as evident from the data and findings presented in the remainder of this memorandum.

Characterization of DNAPL Sites

The guidance document cited below discusses in detail the challenges associated with the characterization and investigation of sites contaminated with DNAPL. "Standard site investigation techniques do not work well to characterize DNAPLs", especially at a Site like this where groundwater is limited and there is no discernible groundwater plume. "Complex and discrete DNAPL migration patterns make it very difficult to delineate subsurface DNAPL using standard investigation techniques. DNAPLs will not be readily apparent in water or soil samples at most sites even if DNAPL is present in the subsurface in significant quantities." Therefore DNAPL presence and distribution needs to be inferred from a lot of data using multiple lines of evidence. "The best method used in DNAPL source area determination may be to use the 'propensity of data' from site characterization efforts. There is no one particular method available to clearly delineate the presence/absence of DNAPL. All data collected during the site investigations and historical site surveys need to be collected and viewed as a whole to determine if there is a potential for DNAPL at the site." \(\)

¹ Interstate Technology & Regulatory Council (ITRC), DNAPL Team. 2003. An Introduction to Characterizing Sites Contaminated with DNAPLs. September. Pages 10, 13, 24.

Although characterization of DNAPL sites can be difficult, the following sections of this memorandum indicate that the data available for the Fields Brook Site, particularly information collected in the last 2 to 3 years, provide multiple lines of evidence that subsurface DNAPL migration from the former Detrex lagoons is continuing and poses a significant threat to Fields Brook.

Detrex Groundwater Interceptor Trench

The groundwater interceptor trench, which is 1400 feet long and consists of three main segments and associated sumps, was installed by Detrex in January 2007 (Figure 1). The objective of the trench was to intercept the southern migration of DNAPL and impacted groundwater from the Detrex lagoon area, where a significant volume of DNAPL is present. The trench is approximately 15 feet in depth and was advanced three feet into the glacial till unit. Groundwater is pumped from the three interceptor trench sumps and then treated (Figure 1). Based on data provided by Detrex, we understand that average groundwater extraction rates at the three sumps (1, 2, and 3, respectively) have been on the order of: 1,250, 750, and 200 gallons per day (gpd) – a total of 2,200 gpd. The water samples collected at the trench sumps indicate the presence of Chlorinated Volatile Organic Compounds (CVOCs), including tetrachloroethene, trichloroethene, 1,2-dichloroethene and 1,1,2,2-tetrachloroethene, at concentrations ranging from 1.1 to 199 µg/L (see Table 1). The detection of these CVOCs is consistent with the composition of the Detrex DNAPL, which has been well characterized and fingerprinted (de maximis, 2005)². As explained in detail below, these flow and concentration data provided by Detrex are highly relevant and indicative of the presence of DNAPL:

- The groundwater extraction rates recorded at the three trench sumps are appreciable for a lacustrine clay system. These relatively high extraction rates would be possible only if there were permeable sand zones in the overburden and lacustrine clay. Such permeable horizons serve as preferential conduits for DNAPL migration in addition to groundwater.
- A comparison of the water quality data collected at the Detrex interceptor trench sumps against data obtained at the North Sewer containment trench sump (a known and significant DNAPL discharge area with visible DNAPL seepage),³ helps place the interceptor trench data in perspective (see Table 1). CVOC concentrations measured at sump #2 of the interceptor trench are on the same order of magnitude as the North Sewer sump, a DNAPL collection area. The similarity in CVOC concentrations at the interceptor trench and the North Sewer sumps is particularly significant because the interceptor trench is an active system (total withdrawal rate of 2,200 gpd over a 1400 foot trench; sump# 2 750 gpd) resulting in significant contaminant dilution, whereas the North Sewer trench is a passive DNAPL collection system (with no groundwater withdrawal). Despite the dilution at the interceptor trench, the similarity in concentrations with the North Sewer sump, indicates that a significant amount of DNAPL is flowing into the interceptor trench (confirmed by calculations results presented below).
- The Detrex groundwater interceptor trench collects all liquids DNAPL, contaminated groundwater and "clean" groundwater that are migrating in the subsurface. Groundwater samples collected at eight locations along the interceptor trench prior to its

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² de maximis, Inc. 2005. Fields Brook Action Group Report of 2005 DNAPL Investigation, Fields Brook Superfund Site, Ashtabula, Ohio. September 30.

³ Significant DNAPL seeps were observed at the North Sewer area from early 2005 onwards, leading to the installation of a passive subsurface collection trench and sump in 2007 by FBAG.

installation did not encounter any contamination (Figure 2), *i.e.*, a majority of the groundwater flowing into the trench is "clean." This clean groundwater mixes with DNAPL globules and DNAPL-impacted groundwater (which flows in *via* narrow preferential conduits into the trench) and results in the observed groundwater concentrations recorded in the water removed at the sumps. Using the water quality and flow rate data collected at the interceptor trench sumps by Detrex, we performed a mass balance calculation to determine the DNAPL and DNAPL-impacted groundwater flow rate entering each segment of the Detrex trench (Attachment A). The mass balance results indicated that up to 2,682 gallons per year of a DNAPL-groundwater mixture, *i.e.*, DNAPL globules/ganglia and groundwater in contact with DNAPL, is flowing into the Detrex trench (Attachment A). The DNAPL flux was highest in trench segment #2, which is consistent with segment #2 being located directly downgradient of the Detrex lagoon area. These results further demonstrate that the Detrex trench is currently intercepting DNAPL, which prior to the installation of this system, was migrating to the brook.

Overall, the groundwater extraction rate and the water quality measured at the Detrex interceptor trench, together with the mass balance analysis results clearly indicate that DNAPL at the Detrex source area continues to feed subsurface migration pathways towards the southern edge of the property.

DNAPL Migration Beyond the Slurry Wall

The following data collected at the DS Tributary indicate that DNAPL has migrated beyond the Detrex slurry wall along the western property boundary.

- DNAPL globules are visible in surficial sediments and a strong odor (characteristics of Detrex DNAPL) is present in the DS Tributary, immediately to the west of State Road. This visual presence of DNAPL was not observable in 2001 or in prior years. Sediment samples collected in the DS Tributary in November 2008 confirm that DNAPL has affected sediment quality since elevated concentrations of CVOCs and other Detrex marker compounds (e.g., hexachlorobenzene and hexachlorobutadiene) were detected (Figures 3 and 4). Furthermore, exceedances of the sediment remedial action levels are now being observed in this area, whereas no exceedances were previously observed and no remediation was necessary (Figure 3).
- Soil and groundwater samples collected near the DS Tributary present strong evidence that Detrex DNAPL is also located in the subsurface in this area.
 - A groundwater sample collected at DPT-10 (8 to 10 ft-bgs) detected extremely high concentrations of the four primary CVOCs: tetrachloroethene (6,580 μg/L), trichloroethene (62,900 μg/L), 1,2-dichloroethene (1,690 μg/L) and 1,1,2,2-tetrachloroethene (11,600 μg/L) ranging from 1% to approximately 50% of their calculated effective solubility limits (Table 3). According to (USEPA, 1992)⁴, the presence of a component of a DNAPL mixture in groundwater at a concentration greater than 1% of its effective solubility, typically indicates the presence of DNAPL. Therefore, the detection of CVOCs at levels up to 50% of their effective solubility limits is very strong evidence that DNAPL is present in the subsurface near the DS Tributary.

⁴ US EPA. 1992. Estimating Potential for Occurrence of DNAPL at Superfund Sites. January.

■ In addition, the soil sample collected at DPT-10 (8 to 10 ft-bgs) also detected elevated CVOC concentrations (277 mg/kg) that are indicative of DNAPL (Figure 4). For example, the trichloroethene and tetrachloroethene concentrations detected at DPT-10 exceed the threshold soil concentration (C_{sat}) above which NAPL is expected to be present (USEPA, 1996)⁵ (Table 2).

Overall, the soil and groundwater quality data collected at DPT-10 clearly demonstrate that this soil boring intercepted a DNAPL pool or ganglion — a rare occurrence when using conventional investigation methods, such as drilling, unless DNAPL presence is widespread. Note, CVOCs were also detected in the subsurface at other locations along State Road, just south of the DS Tributary (Figure 4). Given the proximity of these locations to the DS Tributary DNAPL seepage area and DPT-10 (and the North Sewer DNAPL seepage), these concentrations may be reflective of additional DNAPL migration pathways towards the south (Figure 4).

To summarize, the presence of DNAPL seepage at the DS Tributary, exceedances of sediment remedial action levels in the DS Tributary (none were previously present and no remediation was required in this area), and the presence of elevated subsurface soil and groundwater concentrations indicative of DNAPL near the DS Tributary clearly demonstrate that Detrex DNAPL has migrated beyond the Detrex slurry wall and is manifesting itself at the DS tributary.

DNAPL Manifestation at the North Sewer

The following data collected at and in the vicinity of the North Sewer also indicates that DNAPL from the Detrex property has migrated beyond the western property boundary:

- DNAPL seepage was clearly visible at the North Sewer outfall from 2005 until 2007, when FBAG installed a passive DNAPL subsurface collection trench. The extended period of seepage indicates that the seeps were being fed by a significant DNAPL source indicating the inadequacy of the slurry wall as a source control measure.
- During the North Sewer investigation performed by Detrex in 2006/2007, hexachlorobenzene was detected in sediment samples collected at the North Sewer outfall at concentrations up to 696 mg/kg, which exceeds the remedial action level for hexachlorobenzene (45 mg/kg; Figure 3).
- Elevated concentrations of total CVOCs were also detected in soil samples collected in the vicinity of the North Sewer (e.g., 107 mg/kg at TP6 and 432.5 mg/kg at NSTB-5B and 58.7 mg/kg at NSTB-7) (Figure 4). A comparison of these soil concentrations against C_{sat} values indicates that the cis-1,2-dichloroethene, trichloroethene and tetrachloroethene C_{sat} values were exceeded in samples collected at TP6 (under sewer pipe), NSTB-5B (12 to 14 ft-bgs) and NSTB-7 (10 12 ft-bgs) (Table 2), i.e., DNAPL is present in these samples, which are located north of the Fields Brook floodplain in EU6.
- In June 2008, high CVOC concentrations, (up to 1,195 mg/kg), were found in subsurface soils south of Fields Brook just west of State Road in EU6, on top of the lacustrine clay deposits, *i.e.*, approximately 8 to 10 feet below ground surface (bgs) (Figure 4). These elevated soil concentrations, which exceeded C_{sat} values for VOCs at seven locations (Table 2), are also indication that Detrex DNAPL has migrated along the top of the clay surface and accumulated in this area, a natural low spot in the clay's surface.

⁵ United States Environmental Protection Agency (USEPA). 1996. Soil Screening Guidance: Technical Document. May.

• Geoprobes advanced near the northern State Road Bridge pier prior to brook remediation in 2001 and field observations during the remediation indicate that DNAPL has accumulated at this bridge pier in the upland area (*i.e.*, not in the floodplain area) (Figure 5).

It is important to note that all DNAPL related findings near the North Sewer (C_{sat} exceedances at NSTB-5, NSTB-7, area south of the brook, visual observations in Geoprobes along cross-section G-G') were found approximately 8 to 14 ft-bgs, which generally corresponds to the top of the lacustrine clay layer. This clearly indicates subsurface DNAPL migration along the top of the lacustrine clay layer (and via sand lenses within the clay) – a conclusion that also applies to the DS Tributary area (elevated soil and groundwater concentrations at DPT-10 are at 8 to 10 ft-bgs) and in the area south of the former Detrex lagoons (the Detrex groundwater interceptor trench).

Overall, the data in the vicinity of the North Sewer clearly indicate that Detrex DNAPL has migrated beyond their western property boundary and is manifesting at the North Sewer. Although Detrex needs to collect additional data to define the exact pathway by which the DNAPL is reaching the North Sewer, it is important to note that there is about a 1000 foot gap between the Detrex slurry wall and Detrex groundwater interceptor trench along their western property boundary (Figure 3 and 4).

Table 1
Summary of Detrex Groundwater Interceptor Trench
and North Sewer Sump Data
Fields Brook Superfund Site

	Detrex Gr	oundwater Interc	eptor Trench Dat	a	
		Sump #1 - 125	0 gpd		
		D:	ate		Average
Compound (µg/L)					Concentration
	9/21/2007	11/26/2007	1/3/2008	2/8/2008	(μg/L)
1,1,2,2-Tetrachloroethane	0	0	0	0	-
cis-1,2-Dichloroethylene	0	0	0	0	-
Tetrachloroethylene	5.85	0	1.96	1.13	2.2
Trichloroethylene	7.22	0	2.8	1.57	2.9
		Sump #2 - 750) gpd		
		Da	ate		
Compound (µg/L)					Average
Compound (µg/12)					Concentration
	9/21/2007	11/26/2007	1/3/2008	2/8/2008	(μg/L)
1,1,2,2-Tetrachloroethane	3.45	0	0	1.81	1.3
cis-1,2-Dichloroethylene	199	58	92.8	88.7	109.6
Tetrachloroethylene	25.1	0	0	3.65	7.2
Trichloroethylene	72.1	17.8	21.3	26.6	34.5
		Sump #3 - 200	gpd		
		D:	ate		
Commonad (ug/L)					Average
Compound (µg/L)					Concentration
	9/21/2007	11/26/2007	1/3/2008	2/8/2008	(μg/L)
1,1,2,2-Tetrachloroethane	0	0	0	0	-
cis-1,2-Dichloroethylene	0	0	0	0	-
Tetrachloroethylene	0	0	1.28	1.08	0.6
Trichloroethylene	0	0	1.53	1.5	0.8

North Sewer Sump Data - 0 gpd						
		Average				
Compound (μg/L)	9/28/2007	11/26/2007	2/15/2008	5/1/2008	Concentration (µg/L)	
1,1,2,2-Tetrachloroethane	167	0	0	0	41.8	
1,1,2-Trichloroethane	18.6	0	0	0	4.7	
Chloroform	1.86	0	0	0	0.5	
cis-1,2-Dichloroethylene	NA	44.8	65.2	115	75.0	
Tetrachloroethylene	NA	49.5	33.8	19.9	34.4	
Trichloroethylene	2520	124	95.8	77.8	704.4	

Note:

- Assumed a concentration of zero in the case of non-detections.

Table 2
Soil Saturation Concentration Calculation and List of Exceedances
Fields Brook Superfund Site, Ashtabula, OH

Compound	Effective Solubility (S) ¹ mg/L	Organic Carbon Partition Coefficient (Koc) ² L/kg	Soil Water Partition Coefficient (Kd) L/kg	Henry's Law Constant (H') ² Unitless	Soil Saturation Concentration (C _{sat}) ³ mg/kg	Sample Locations with C _{sat} Exceedances
						TP6 (3.6 mg/kg), MLSS-02 (3.3 mg/kg), MLSS-04 (30 mg/kg), MLSS-14 (6.3
Cis-1,2-Dichloroethene	11.2	43.8	0.0876	0.167	2.29	mg/kg), MLSS-15 (4.7 mg/kg)
Trichloroethene	673.3	. 67.7	0.14	0.403	185.63	NSTB-5B (257 mg/kg), MLSS-15 (600 mg/kg), DPT-10 (252 mg/kg)
						NSTB-5B (175 mg/kg), TP6 (83.3 mg/kg), NSTB-7 (42.3 mg/kg), MLSS-9 (84 mg/kg), MLSS-10 (36 mg/kg), MLSS-13 (18 mg/kg), MLSS-14 (9.6 mg/kg), MLSS-
Tetrachloroethene	13.3	107	0.214	0.724	5.14	15 (590 mg/kg), DPT-10 (24.7 mg/kg)
1,1,2,2-Tetrachloroethane	1059.6	107	0.214	0.015	334.30	

Fraction of organic carbon (foc) 0.002 Bulk Density (ρ) $1.50\,$ g/ml Water-filled Porosity (θ w) 0.15 Air-filled Porosity (θ a) 0.15

 $Csat = (S/\rho) * (Kd * \rho + \theta w + H' * \theta a)$

Source:

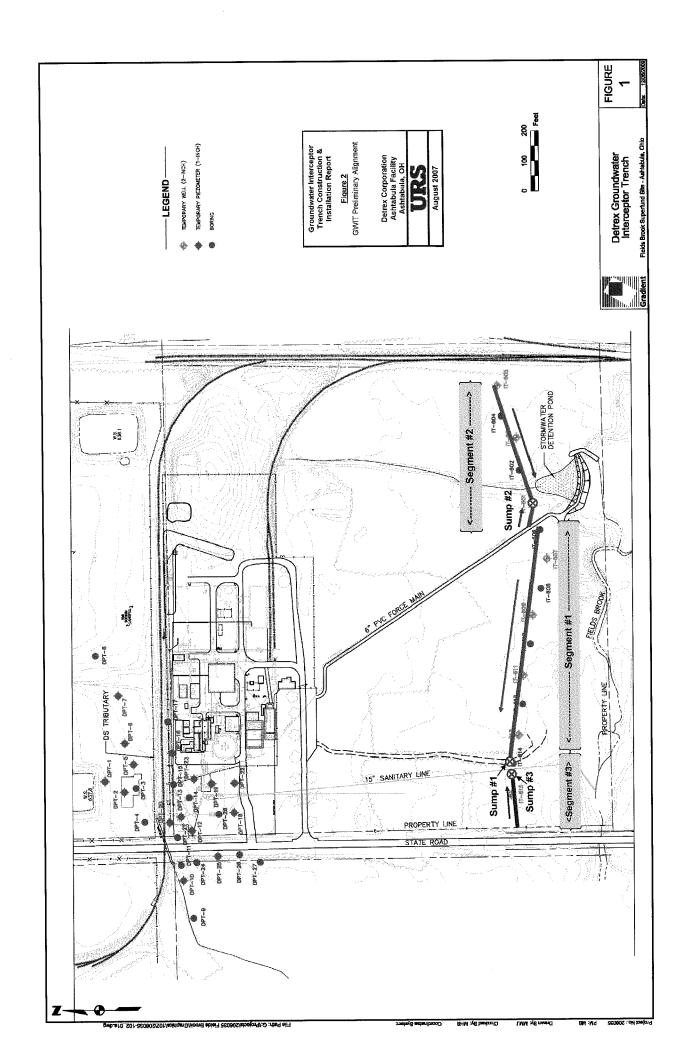
- 1) Effective solubility calculations are presented in Attachment A.
- 2) Risk Assessment Information System: http://rais.ornl.gov
- 3) United States Environmental Protection Agency (USEPA). 1996. Soil Screening Guidance: Technical Document. May.

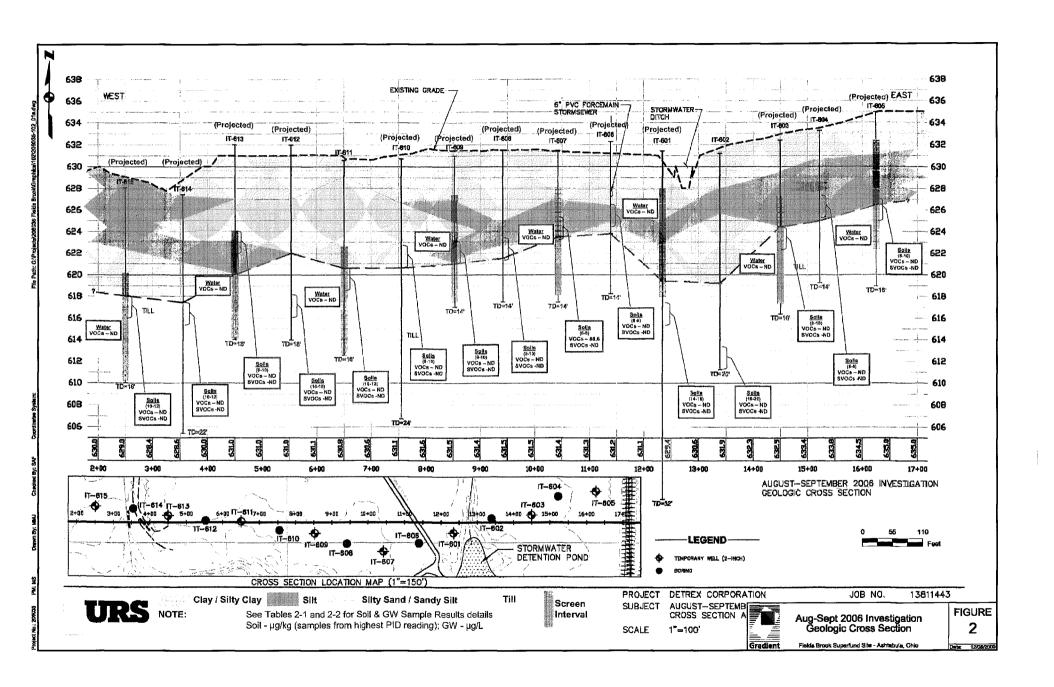
Table 3
Comparison of CVOC Detections in DPT-10 Groundwater and Effective Solubility

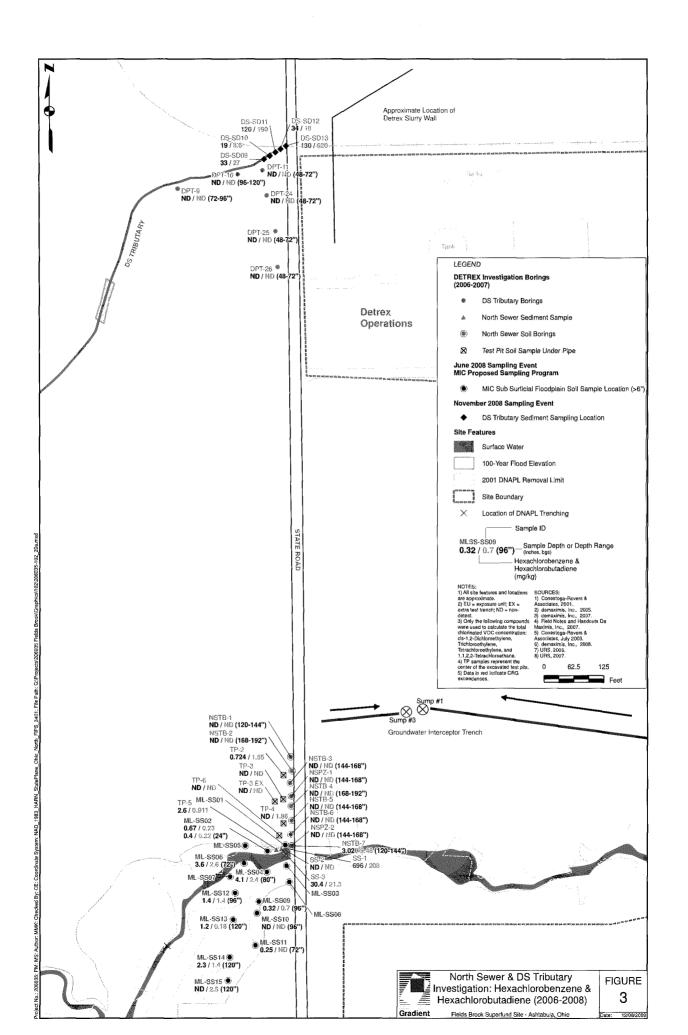
Compound	Concentration in Groundwater (µg/L)	Effective Solubility $\left(\mu g/L\right)^{1}$	Ratio of Groundwater Concentration to Effective Solubility
1,2-Dichloroethene	1,690	11,200	0.2
Trichloroethene	62,900	673,300	0.1
Tetrachloroethene	6,580	13,300	0.5
1,1,2-Trichloroethane	1,610	300	5.4
1,1,2,2-Tetrachloroethane	11,600	1,059,600	0.01

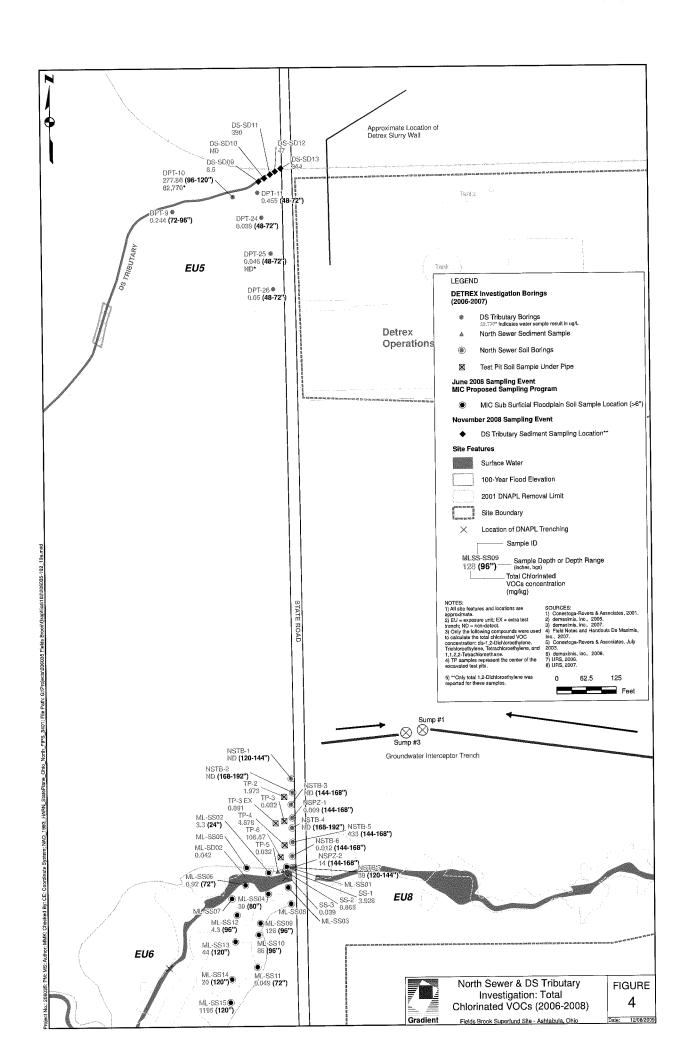
Note:

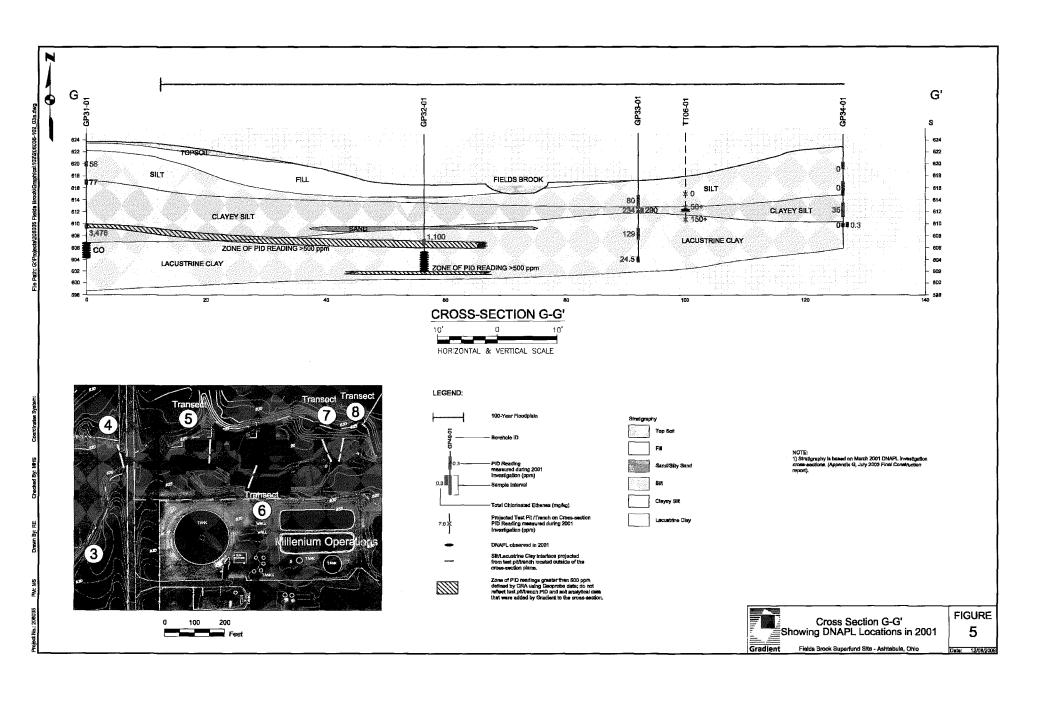
¹⁾ Effective solubility calculations are presented in Attachment A.











Attachment A Detrex Groundwater Interceptor Trench Calculations

This attachment describes the calculations performed to determine the nature and volume of contamination recovered by the Detrex groundwater interceptor trench, using available water quality and flow data, and the following assumptions:

- The groundwater flux into the trench is a combination of DNAPL-groundwater mixture, (*i.e.*, DNAPL globules and groundwater in contact with DNAPL) and "clean" groundwater (*i.e.*, groundwater that has not been in contact with the DNAPL.
- The maximum concentration of a contaminant in the DNAPL-impacted groundwater is equal to the effective solubility of that contaminant in water. Given that the Detrex DNAPL is a mixture of a dozen organic compounds, Raoult's Law dictates that the effective solubility of each contaminant in groundwater that has been in contact with the DNAPL is proportional to the mole fraction of that contaminant in the mixture.
- No contaminants were detected in the "clean" groundwater. This assumption is reasonable, given the absence of VOCs in the groundwater samples collected along the length of the trench prior to its installation (see Figure 2).

In order to determine the flux of DNAPL-groundwater mixture into each segment of the trench, we used a simple mass balance approach represented by the following equation:

$$(V_{W-DNAPL} \times C_{W-DNAPL}) + (C_{gw} \times V_{gw}) = (C_{Sump} \times V_{Total})$$

Where:

 $V_{W-DNAPL}$ = Average flux of DNAPL-groundwater mixture (*i.e.*, DNAPL globules and groundwater in contact with DNAPL) into each segment of the trench (gpd)

 $C_{W-DNAPL}$ = Effective solubility of the contaminant in groundwater for Detrex DNAPL (mg/L). As shown in Table A-1, the effective solubility of each constituent of the DNAPL mixture was determined by multiplying the mole fraction of the constituent in the DNAPL mixture by its pure form solubility limit (Mercer and Cohen, 1990)¹.

 C_{ow} = Average contaminant concentration in "clean" groundwater, assumed to be zero mg/L.

 V_{gw} = Average flux of "clean" groundwater into each segment of the trench (gpd)

 C_{Sump} = Average concentration of the contaminant in sump water (mg/L). For each segment of the trench, we calculated the average concentration of the contaminant using sump water quality data collected by Detrex in September 2007, November 2007, January 2008, and February 2008.

 V_{Total} = Average flux recorded at each sump by Detrex (gpd).

¹ Mercer, JW; Cohen, RM. 1990. "Review of immiscible fluids in the subsurface: Properties, models, characterization and remediation." *J. Contam. Hydrol.* 6:107-163.

Given the assumption that the "clean" groundwater does not contain detectable levels of contamination (URS, 2006), i.e., $C_{gw} = 0$, the equation can be revised as follows:

$$V_{W-DNAPL} = \frac{(C_{Sump} \times V_{Total})}{C_{W-DNAPL}}$$

The calculations to determine the flux of DNAPL-groundwater mixture into the three segments of the trench are presented in Table A-2. Note, the calculations were only performed for the four VOCs (tetrachloroethene, trichloroethene, 1,2-dichloroethene and 1,1,2,2-tetrachloroethene) that were detected in sump water samples and are the primary constituents of the Detrex DNAPL mixture.

Table A-1 Effective Solubility Calculations for Detrex DNAPL Fields Brook Superfund Site, Ashtabula, OH

Compound	Composition of Detrex DNAPL from MW-07S (µg/kg) 1	Solubility Limit (mg/L)	Molecular Weight (g/mole)	Mole Fraction	Effective Solubility (mg/L) ²
1,1,2-Trichloroethane	150,000	1100	133,41	0.0003	0.3
1,2-Dichlorobenzene	430,000	80	147	0.001	0.1
Chloroform	680,000	7950	119.4	0.001	10.8
Tetrachloroethylene	45,000,000	206	165.8	0.065	13.3
Trichloroethylene	290,000,000	1280	131.4	0.526	673.3
1,2-Dichloroethylene (total)	1,300,000	3,500	96.94	0.003	11.2
1,1-Dichloroethene	480,000	2,420	96.94	0.001	2.9
1,1,2,2-tetrachloroethane	260,000,000	2,870	167.85	0.369	1059.6
Hexachloroethane	20,000,000	50	236.74	0.020	1.0
Hexachlorobutadiene	8,500,000	3	260,76	0.008	0.0
Hexachlorobenzene	4,600,000	0.006	284.78	0.004	0.0
4-chloro-3-methylphenol	950,000	3,830	142.59	0.002	6.1

Note:

- 1. de maximis, Inc. 2005. Fields Brook Action Group Report of 2005 DNAPL Investigation, Fields Brook Superfund Site, Ashtabula, Ohio. September 30. 2. Effective Solubility = Solubility Limit x Initial Mole Fraction

Table A-2
Detrex Groundwater Interceptor Trench Calculations
Fields Brook Superfund Site, Ashtabula, OH

Sump #1

Total Flux of DNAPL-groundwater mixture into Segment#1 (Vtotal) = 1250 gpd

Compound	Average Measured Concentration in Sump 1 Water	Effective Solubility in Groundwater	Flux of DNAPL-groundwater mixture into Segment #1	Flux of DNAPL-groundwater mixture into Segment #1
	C _{sump} (mg/L)	C _{W-DNAPL} (mg/L)	V _{W-DNAPL} (gpd) ¹	V _{W-DNAPL} (gallons per year)
Tetrachloroethylene	0.002	13.3	0.210	77
Trichloroethylene	0.003	673.3	0.005	2
1,2-Dichloroethylene (total)	0.000	11.2	0.000	0
1,1,2,2-Tetrachloroethane	0.000	1059.6	0.000	0

Sump #2

Total Flux of DNAPL-groundwater mixture into Segment#2 (Vtotal) = 750 gpd

Compound	Average Measured Concentration in Sump 2 Water	1	Flux of DNAPL-groundwater mixture into Segment #2	Flux of DNAPL-groundwater mixture into Segment #2
	C _{sump} (mg/L)	C _{W-DNAPL} (mg/L)	V _{W-DNAPL} (gpd) ¹	V _{W-DNAPL} (gallons per year)
Tetrachloroethylene	0.007	13.3	0.405	148
Trichloroethylene	0.034	673.3	0.038	14
1,2-Dichloroethylene (total)	0.110	11.2	7.349	2682
1,1,2,2-Tetrachloroethane	0.001	1059.6	0.001	0.3

Sump #3

Total Flux of DNAPL-groundwater mixture into Segment#3 (Vtotal) = 200 gpd

Compound	Average Measured Concentration in Sump 3 Water	1	Flux of DNAPL-groundwater mixture into Segment #3	Flux of DNAPL-groundwater mixture into Segment #3
	C _{sump} (mg/L)	C _{W-DNAPL} (mg/L)	V _{W-DNAPL} (gpd) ¹	V _{W-DNAPL} (gallons per year)
Tetrachloroethylene	0.001	13.3	0.009	3
Trichloroethylene	0.001	673.3	0.0002	0.1
1,2-Dichloroethylene (total)	0.000	11.2	0.0000	0
1,1,2,2-Tetrachloroethane	0.000	1059.6	0.000	0

Note:

1) $V_{W-DNAPL} = (C_{sump} * V_{total})/C_{W-DNAPL}$

Attachment 5

Soil, Sediment, and Groundwater Benchmarks

Gradient and FBAG have used two EPA-approved contaminant concentration benchmarks (C_{sol} and C_{sal}) to evaluate data collected at Fields Brook. In the current memo, a third soil concentration benchmark, C_{mobile} , is introduced to further evaluate site data. Each of these benchmarks is described in more detail below along with the specific applications of these benchmarks to site-specific data.

Effective Aqueous Solubility Limit - Csol

The effective aqueous solubility limit defines equilibrium aqueous solubility limit for individual VOC/SVOCs in a DNAPL mixture. Two factors affect this solubility limit:

- The pure-phase aqueous solubility— Each compound in a DNAPL mixture has its own unique aqueous solubility limit when the pure phase compound dissolves in pure water.
- DNAPL Composition When DNAPL contains more than one VOC/SVOC, the presence of multiple compounds inhibits the dissolution of other VOC/SVOCs in the mixture. As a result, the solubility of a compound in a DNAPL mixture is always lower than its pure-phase solubility. This phenomenon is widely known as Raoult's law, which states that the effective aqueous solubility of a compound in a DNAPL mixture is equal to its mole fraction in the DNAPL mixture times its pure-phase aqueous solubility (Equation 1).

$$C_{sol} = m_i C_i \tag{1}$$

 C_{sol} – the effective aqueous solubility limit

 m_i – the mole fraction of an individual VOC/SVOC in a DNAPL mixture

 C_i – the pure-phase aqueous solubility of an individual VOC/SVOC

Due to the sparse and tortuous nature of subsurface DNAPL migration, EPA recommends using 1% of a compound's effective aqueous solubility limit (C_{sol}) as an indicator of DNAPL presence (USEPA, 1992)¹. Gradient previously calculated the effective aqueous solubility limits for several Detrex marker compounds and these limits are reproduced in Attachment 2.

Soil Saturation Concentration - Csat

The C_{sat} concept is based on a soil partitioning theory that assumes DNAPL can distribute across several phases in a soil or be present as a pure phase liquid. It applies to individual VOC/SVOCs in granular soils where significant NAPL can accumulate in the pore spaces (e.g. in gravel, sand, and silt) and assumes that DNAPL is evenly distributed through the soil. In these instances, VOC/SVOCs may reside in four different phases in the soil (expressed symbolically in Equation 2):

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- Adhered to the surface of soil particles (adsorbed phase)
- Dissolved in water contained in the soil pore spaces (dissolved phase)
- Evaporated into the air contained in soil pore spaces (vapor phase)

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¹ US EPA. 1992. Estimating Potential for Occurrence of DNAPL at Superfund Sites. January.

Accumulated as a non-aqueous phase liquid (NAPL) in the soil pore spaces (NAPL phase)

$$C_{sat} = \frac{C_{sol}}{\rho_b} \left(K_d \rho_b + \theta_w + H \theta_a \right)$$
adsorbed phase dissolved phase vapor phase

 C_{sat} – soil saturation concentration, above which indicates DNAPL presence

 C_{sol} – effective aqueous solubility limit (described above)

 ρ_b – soil bulk density

 K_d – adsorption coefficient for VOC/SVOCs to soil

 θ_w – water-filled porosity

 θ_a – air-filled porosity

H – Henry's law constant (describing the equilibrium between dissolve VOCs and VOC vapors)

 C_{sat} is the bulk soil VOC concentration where adsorption, dissolution, and vaporization are at their upper thresholds, *i.e.* no more VOC can be held by the soil without the presence of NAPL. Thus, Csat exceedances merely indicate the presence of NAPL in granular soils (*e.g.* gravel, sand and silt). In clayey soils, such as those found at Fields Brook, the practical application of C_{sat} theory is limited by two factors:

- DNAPL flows through clay fractures rather than the extremely small pore spaces in the clay. C_{sat} calculations are based on DNAPL accumulation in pore spaces, not in fractures and therefore, the theory is not appropriate for the fractured clay soils at the site.
- Soil sampling methods homogenize clean clay soil with DNAPL-contaminated fractures.
 VOC concentrations (and DNAPL) get diluted to low concentrations and makes comparisons to C_{sat} inappropriate, since the C_{sat} theory inherently assumes that VOCs are distributed evenly throughout soil pore spaces.

As a result, the C_{sat} calculation is only appropriate for sand and gravel seams at Fields Brook and Gradient previously calculated these values for Detrex DNAPL marker compounds (Attachment 2; Gradient 2008. 208-7101). A better metric for inferring DNAPL presence and mobility in fractured clay is the C_{mobile} concept, which is described below.

Mobile DNAPL Soil/Sediment Concentration Threshold - Cmobile

The C_{mobile} concept is based on observations indicating that NAPL spontaneously mobilizes (drains under its own weight) when it fills a certain percentage of the fractures or pore spaces in a soil (Wiedemeier *et al.* 1999. 200-2791). Because C_{mobile} is applicable to fractures, it is a more appropriate metric to use in the fractured clays found at Fields Brook. The information required to estimate C_{mobile} is readily available and includes the following:

• The fraction of soil volume occupied by fractures (fracture pososity, n) – Although this has not been measured at Fields Brook, Gradient selected a fracture porosity of 0.00025, a reasonable upper bound for fractured clay settings (Pankow and Cherry, 1996. 97-3259).

- The percentage of fractures/pore spaces that must be filled to initiate NAPL flow (residual NAPL saturation, S) Residual NAPL saturation ranges from 5% to 50% (Newell and Ross, 1992)² and to be conservative, Gradient selected the lower end of this range.
- The densities of NAPL (ρ_n , assumed 1.4 g/mL) and water (ρ_n , equal to 1 g/mL).

$$C_{mobile} = nS \frac{\rho_n}{\rho_w} \tag{3}$$

With the above assumptions, C_{mobile} for the fractured clay at Fields Brook is 13 mg/kg total VOCs. Whereas exceedances of C_{sat} and C_{sol} indicate the presence of NAPL globules or ganglia, exceedances of C_{mobile} indicate the presence of mobile NAPL. Another major difference is that C_{mobile} applies to total VOCs rather than individual VOCs. This is due to the focus of C_{mobile} being on NAPL rather the C_{sat} and C_{sol} focus on individual NAPL components.

There are also several caveats to the use of C_{mobile} at the Fields Brook site:

- *C*_{mobile} has been broadly applied to all soil samples, even those in sandy soil strata. This may overestimate the presence of mobile DNAPL in certain soil samples. The vast majority of soil samples are in clay soils and the concentrations of total VOCs are sufficiently high that this issue does not affect the analysis that Gradient and FBAG have performed.
- Total VOC concentrations were compared to the C_{mobile} benchmark, although SVOCs would also contribute to the mass of mobile DNAPL in soils. Because SVOCs (*i.e.* hexachlorobenzene and hexachlorobutadiene) are major components of Detrex DNAPL and were not considered, this provides a degree of conservatism to the analysis.
- Site specific measurements of fracture porosity (n) and residual DNAPL saturation (S) were not available. As a result, this analysis is best used as an indicator of areas of concern that require further evaluation. Soils that exceed the C_{mobile} threshold are certainly of concern, but soils below the threshold do not mean that mobile DNAPL is absent. This is because soil samples are collected at discrete intervals from borings and may not encounter a DNAPL-filled fracture. That is, finding DNAPL at the Fields Brook site is "hit-or-miss" due to the sparsely distributed and tortuous nature of DNAPL migration.

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² Newell, C.J. and Ross, R.R. 1992. Estimating Potential for Occurrence of DNAPL at Superfund Sites. US EPA, R.S. Kerr Environmental Research Laboratory. January 1992.